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**AFRPL-68-47**

March 25, 1968

Technical Progress Report No. 4 — Final

**SYNTHESIS OF ENERGETIC OXIDIZERS (U)**

By: W. E. TOLBERG    R. T. REWICK    G. R. ZEILENGA  
J. A. NEFF    M. P. DOLDER    M. E. HILL

*Prepared for:*

AIR FORCE ROCKET PROPULSION LABORATORY-  
RESEARCH AND TECHNOLOGY DIVISION  
AIR FORCE SYSTEMS COMMAND  
EDWARDS AIR FORCE BASE, CALIFORNIA

CONTRACT F 04611-67-C-0002

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SRI Project FRU-6200

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## FOREWORD

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This final report was prepared by Stanford Research Institute, Menlo Park, California, for the Air Force Rocket Propulsion Laboratory, Edwards Air Force Base, California. The report covers work from August 1, 1966 to September 30, 1967, under Air Force Contract F 04611-67-C-0002. This is a continuation of the work begun under Contract AF 04(611)-9370. Scientists working on the program include M. E. Hill, project supervisor, W. E. Tolberg, R. T. Rewick, G. R. Zeilenga, J. A. Neff, and M. P. Dolder; C. A. Crutchfield and Anna Longwell are responsible for analytical work. The technical consultation of Dr. H. Taube, of Stanford University, is gratefully acknowledged.

The Air Force Rocket Propulsion Laboratory Contract Monitor is Dr. Frank Roberto/RPCS.

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This technical report has been reviewed and is approved.

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W. H. Ebelke, Colonel, USAF  
Chief, Propellant Division



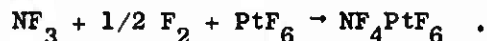
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## ABSTRACT

(C) Synthesis of  $\text{NF}_4^+$  salts has been carried out by two general methods. Direct synthesis reactions of  $\text{NF}_3$ ,  $\text{F}_2$ , and a series of Lewis acids at high pressure and moderately elevated temperatures have been used to produce a series of  $\text{NF}_4^+$  salts having fully fluorinated anions. Metathesis reactions in liquid HF have been used to produce a number of new  $\text{NF}_4^+$  salts including some with oxygen-containing anions.

(C) The rate of reaction to form  $\text{NF}_4^+$  salts in direct synthesis depends on the acidity of the Lewis acid. Thus,  $\text{SbF}_5$  forms  $\text{NF}_4\text{SbF}_6$  in good yield,  $\text{AsF}_5$  produces the arsenate in moderate yield,  $\text{PF}_5$  forms  $\text{NF}_4\text{PF}_6$  in very low yield, and  $\text{BF}_3$  produces only a trace of  $\text{NF}_4\text{BF}_4$ . It was concluded that compounds less acidic than  $\text{BF}_3$  in HF would be unlikely to form  $\text{NF}_4^+$  salts by direct synthesis. This was confirmed when  $\text{ClF}_3$  and  $\text{ClF}_5$  did not yield the corresponding salts,  $\text{NF}_4\text{ClF}_4$ , or  $\text{NF}_4\text{ClF}_6$ , on heating  $\text{NF}_3$ ,  $\text{F}_2$ ,  $\text{ClF}_3$ , and  $\text{ClF}_5$  at high pressure for extended periods of time.

(C) In addition to  $\text{NF}_4\text{SbF}_6$ ,  $\text{NF}_4\text{AsF}_6$ , and  $\text{NF}_4\text{PF}_6$ , a fourth salt,  $\text{NF}_4\text{PtF}_6$ , was formed by direct synthesis in the reaction:

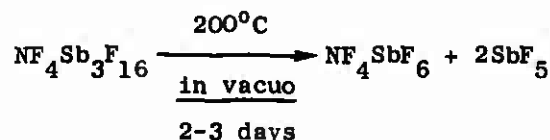
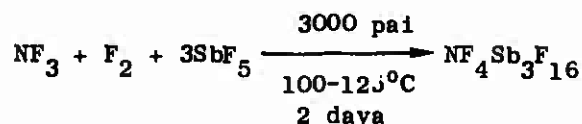


This salt was characterized by nmr and infrared spectroscopy, hydrolysis, and elemental analysis of the hydrolysate.

(U)  $\text{NF}_4\text{SbF}_6$  has proved to be the most useful in metathesis reactions. Its synthesis is complicated by the formation of varying amounts of the complex fluoroantimonate anions,  $\text{Sb}_2\text{F}_{11}^-$  and  $\text{Sb}_3\text{F}_{16}^-$ , as well as formation of contaminants formed by reaction of  $\text{F}_2$  and  $\text{SbF}_5$  with the Monel reaction vessel. The optimum conditions found for synthesis of  $\text{NF}_4\text{SbF}_6$  involve:

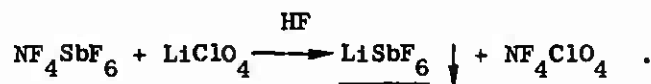
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Products ranging in purity from 96 to 99.5% have been obtained. Monel-antimonate impurities were removed by dissolving  $\text{NF}_4\text{SbF}_6$  in HF and filtering out the insoluble metal salts. Monel antimonate impurities are mainly  $\text{Ni}(\text{SbF}_6)_2$  and  $\text{Cu}(\text{SbF}_6)_2$ . Other components in Monel metal comprise 2.5% or less of the metal and their presence in the impurities (except for Si which has been detected as small amounts of  $\text{SiF}_4$ ) has not been confirmed by us.

(C) Fully characterized  $\text{NF}_4\text{SbF}_6$  has been used as a reagent in a number of metathesis reactions forming new salts. A typical reaction is:



Similar reactions have been used to form  $\text{NF}_4\text{HF}_2$ ,  $\text{NF}_4\text{SO}_3\text{F}$ ,  $\text{NF}_4\text{NO}_3$ , and  $\text{NF}_4\text{BF}_4$ . The perchlorate decomposes to  $\text{NF}_3$  and  $\text{FClO}_4$  above  $-27.5^\circ\text{C}$ , the bifluoride is unstable at  $-44^\circ\text{C}$  and above, the fluorosulfonate is unstable at  $-78^\circ\text{C}$  and above, the nitrate is decomposed in HF solution, but  $\text{NF}_4\text{BF}_4$  is quite stable.

(C)  $\text{NF}_4\text{CN}$  could not be formed owing to decomposition of the alkali metal cyanide to HCN in liquid HF and to the reaction of cyanide with the inter-halogen solvent  $\text{BrF}_5$ . The similar decomposition of  $\text{K}_2\text{SiF}_6$  in HF led to an attempt to synthesize  $(\text{NF}_4)_2\text{SiF}_6$  in  $\text{BrF}_5$ . No reaction occurred on mixing  $\text{NF}_4\text{SbF}_6$  with  $\text{K}_2\text{SiF}_6$  in  $\text{BrF}_5$ . The lack of reaction may indicate that one or both of the starting reagents dissolved without dissociation into ionic species.

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(C) Several alkali metal salts of the  $\text{ClF}_4^-$  and  $\text{BrF}_6^-$  anions were synthesized. In HF, these decompose to form alkali metal bifluorides and the corresponding interhalogen. They are, however, moderately soluble in  $\text{BrF}_5$ . It is expected that this solvent will permit determining whether the salts  $\text{NF}_4\text{ClF}_4$  and  $\text{NF}_4\text{BrF}_6$  can be synthesized.

(C) An effort was made to synthesize  $\text{NF}_4\text{BF}_4$  in a purity sufficient for determining heats of formation. The highest purity obtained was a sample containing 92%  $\text{NF}_4\text{BF}_4$  and 8%  $\text{NF}_4\text{SbF}_6$ .

(U) A number of solubility studies were carried out in support of work on metathesis reactions. Solubilities of a number of pertinent compounds in HF,  $\text{BrF}_5$ ,  $\text{IF}_5$ , and  $\text{BrF}_3$  are reported and discussed.

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## I INTRODUCTION

(U)This report summarizes progress between August 1, 1967, and September 30, 1967, on research concerned with the synthesis of energetic oxidizers. The objectives of the work are to study the chemistry of the  $\text{NF}_4^+$  cation and to apply this chemistry to the synthesis of solid inorganic oxidizers.

(U)This program is a continuation of research carried out under Contract AF 04(611)-9370, which involved studies of the interactions of  $\text{NF}_3$  and  $\text{F}_2$  with the fluoride acceptors  $\text{SbF}_5$ ,  $\text{AsF}_5$ , and  $\text{HF}$ . The results of these studies included the synthesis and characterization of the salts  $\text{NF}_4\text{SbF}_6$ ,  $\text{NF}_4\text{Sb}_2\text{F}_{11}$ ,  $\text{NF}_4\text{Sb}_3\text{F}_{16}$ , and  $\text{NF}_4\text{AsF}_6$ , as well as the probable synthesis of  $\text{NF}_2^+\text{Sb}_2\text{F}_{11}^-$ . Because of the high yields of reactions that form  $\text{NF}_4^+$  salts and the apparent high stability of  $\text{NF}_4^+$  compared with  $\text{NF}_2^+$ , study of the chemistry of  $\text{NF}_4^+$  has been emphasized in this continuing work.

(U)During the current contract period, we have studied the synthesis of  $\text{NF}_4^+$  salts by means of two general approaches. The first of these, the direct synthesis approach, involved the temperature/pressure activated reactions of  $\text{NF}_3$  and  $\text{F}_2$  with a series of Lewis acids. The second, metathesis reactions in liquid  $\text{HF}$ , were used to synthesize more or less energetic salts. In addition, we have studied a number of systems in the interhalogen solvents  $\text{BrF}_5$  and  $\text{IF}_5$  in which it is possible that metathetical reactions can take place.

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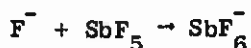
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## II DISCUSSION

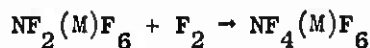
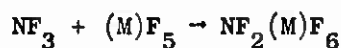
### A. Direct Synthesis Reactions of $\text{NF}_4^+$ Salts

(C)The first reaction in which an  $\text{NF}_4^+$  salt was synthesized was the reaction of  $\text{NF}_3$  and  $\text{F}_2$  with  $\text{SbF}_5$  to form  $\text{NF}_4\text{SbF}_6$ . From this it seemed clear that a series of  $\text{NF}_4^+$  salts could be directly synthesized from  $\text{NF}_3$ ,  $\text{F}_2$ , and a series of Lewis acids. This conclusion is true provided that the Lewis acid involved is sufficiently acidic. In the series  $\text{SbF}_5$ ,  $\text{AsF}_5$ ,  $\text{PF}_5$ ,  $\text{BF}_3$ ,  $\text{ClF}_5$ , and  $\text{ClF}_3$ , we found that acidity with respect to HF was the key factor in the rate of production of  $\text{NF}_4^+$  salts. Thus the rate of formation fell off rapidly as we proceeded from  $\text{SbF}_5$  to  $\text{ClF}_3$ . Good yields were obtained only with  $\text{SbF}_5$  and  $\text{AsF}_5$ , while  $\text{PF}_5$  yielded a few tenths of a gram and  $\text{BF}_3$  yielded only a trace. Attempts to form  $\text{NF}_4\text{ClF}_4$  and  $\text{NF}_4\text{ClF}_6$  produced no evidence of  $\text{NF}_4^+$  salt formation. This is consistent with the fact that  $\text{ClF}_3$  and  $\text{ClF}_5$  are basic or slightly basic in HF.

(C)In a direct synthesis reaction which differed from the above,  $\text{PtF}_6$  was used as the anion precursor and was found to form  $\text{NF}_4\text{PtF}_6$  very slowly. The anion-forming reaction is essentially  $\text{PtF}_6 + e^- \rightarrow \text{PtF}_6^-$  and thus differs from the classical Lewis acid concept wherein, for example,

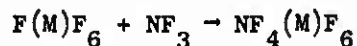
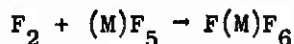


(C)We are not certain of the mechanism by which  $\text{NF}_4^+$  is formed. Two alternatives occur and either can account for the relatively slow formation of  $\text{NF}_4^+$  salts:



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or



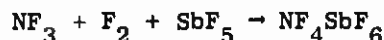
where M may be antimony, arsenic, phosphorus, or boron.

(U)The concentration of either intermediate must be small during reaction. The system  $\text{NF}_3/\text{SbF}_5$  was heated at  $200^\circ\text{C}$  for two days and resulted in formation of a very small amount of solid product. The product contained  $\text{NF}_4^+$  salt as well as a material that hydrolyzed to yield nitrogen oxides. Formation of the latter could have been due to the presence of an  $\text{NF}_2^+$  salt. It could also have been the result of disproportionation of  $\text{NF}_3$  into  $\text{N}_2\text{F}_4$  and  $\text{F}_2$ , the  $\text{N}_2\text{F}_4$  forming a complex with  $\text{SbF}_5$ . Thus no clearcut evidence as to the formation of  $\text{NF}_2^+$  salts was obtained from this brief study, but the implication was clear that the  $\text{NF}_2^+$  salt could serve as the limiting reagent in the reaction. We have not studied the possible  $\text{F}_2/\text{SbF}_5$  interaction.

(C)Because the systems involving reaction of  $\text{NF}_3$ ,  $\text{F}_2$ , and a Lewis acid differ, each will be described below.

## 1. (U) $\text{NF}_4\text{SbF}_6$

(U)The reaction to form  $\text{NF}_4\text{SbF}_6$  can be written:



However, this reaction is complicated by the behavior of  $\text{SbF}_5$ , which tends strongly to associate with itself or with  $\text{SbF}_6^-$ . As a result, depending on the temperature and heating time, the product may consist of  $\text{NF}_4\text{SbF}_6$ ,  $\text{NF}_4\text{Sb}_2\text{F}_{11}$ ,  $\text{NF}_4\text{Sb}_3\text{F}_{16}$ , or mixtures of these.

(U)At  $80^\circ\text{C}$ , 2000-3000 psi, and a heating time of two days, the product is  $\text{NF}_4\text{Sb}_3\text{F}_{16}$  with some unreacted  $\text{SbF}_5$ . At  $100^\circ$  to  $125^\circ\text{C}$  with the same pressure and heating time, the product is almost exclusively  $\text{NF}_4\text{Sb}_3\text{F}_{16}$ . At higher temperatures, the product contains  $\text{NF}_4\text{Sb}_2\text{F}_{11}$  and  $\text{NF}_4\text{SbF}_6$ . The

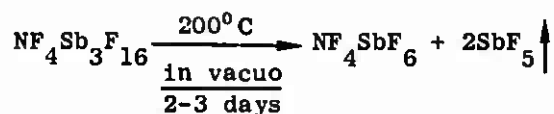
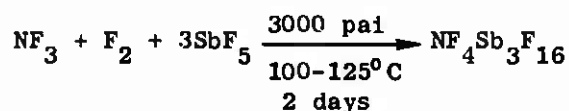
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product obtained at 200°C, 2000-3000 psi, and a heating time of one day, is largely  $\text{NF}_4\text{Sb}_2\text{F}_{11}$  with a few percent of  $\text{NF}_4\text{SbF}_6$ .

(U) From analysis of a large number of preparations, we have concluded that the method of preparation yielding the purest final product of  $\text{NF}_4\text{SbF}_6$  is the following:



(U) The product from the first step of the reaction sequence is isolated from the reactor by cutting it open with a hacksaw within a drybox and scraping out the salt, which forms as a melt in the bottom of the reactor. The product is not sensitive to impact nor to any of these manipulations.

(U) The  $\text{NF}_4\text{Sb}_3\text{F}_{16}$  is ground to a fine powder in a sapphire mortar and placed in a flanged vessel. Conversion to  $\text{NF}_4\text{SbF}_6$  is carried out by heating the vessel to 200°C while evacuating it through a dry ice-cooled trap. When  $\text{SbF}_5$  is no longer collected in the trap, the reaction is complete.

(U) Occasionally,  $\text{NF}_3$  is evolved during the heating procedure. This has been attributed to reaction of the  $\text{NF}_4^+$  salt with the Monel vessel. The metal vessel is usually pretreated with  $\text{F}_2$  under one to two atmospheres of pressure at 200°C. The pretreatment minimizes the reaction of  $\text{NF}_4^+$  salt with the container.

(U) The  $\text{NF}_4\text{SbF}_6$  prepared according to the above procedure is found on analysis to be from 96 to 99.5% pure, the impurities being Monel- $\text{SbF}_6^-$  salts. These impurities are relatively insoluble in HF and can be removed by extracting the very soluble  $\text{NF}_4\text{SbF}_6$  with liquid HF. The amount of impurities has been reduced to about 0.5% by weight by this extraction procedure.

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## 2. (U) $\text{NF}_4\text{AsF}_6$

(U)Initially, both  $\text{NF}_4\text{SbF}_6$  and  $\text{NF}_4\text{AsF}_6$  were prepared in reactions that included liquid HF along with  $\text{NF}_3$ ,  $\text{F}_2$ , and the Lewis acid. The presence of liquid HF resulted in extensive corrosion of the reaction vessels and in products that contained large amounts of Monel fluorides and hexafluoroarsenates and antimonates. In the  $\text{NF}_4\text{AsF}_6$  synthesis, there was an additional problem in that, at the reaction temperature of  $200^\circ\text{C}$ , the Monel arsenates appeared to be volatile and sublimed to cooler portions of the reactor, plugging the inlet line. This sublimation also resulted in removal of the otherwise passive coating of Monel salts from the heated portion of the reactor, causing continued exposure of reactive metal surface. This behavior resulted in formation of a large amount of Monel-arsenate salts during the reaction. From these observations it was clear that the reaction temperature should be held below the temperature at which sublimation occurred. In addition, it was obvious that since  $\text{NF}_4\text{SbF}_6$  formed in relatively high purity in the absence of HF, liquid HF should be omitted from the reaction.

(U)For these reasons, a mixture of  $\text{NF}_3$ ,  $\text{F}_2$ , and  $\text{AsF}_5$  was heated at a temperature of  $125^\circ\text{C}$  at an initial pressure of 2500 psi for ten days. In contrast to the preparation of  $\text{NF}_4\text{SbF}_6$  which is formed at the bottom of the reactor,  $\text{NF}_4\text{AsF}_6$  is found uniformly distributed on the walls of the reactor. The fine white powder is scraped off the walls and isolated. A typical preparation yields about six grams of product.

(U)Because the product is formed on the walls and must be isolated by scraping it out, more impurities from the vessel have been found in the  $\text{NF}_4\text{AsF}_6$ . The product is typically about 93% pure, the balance consisting of Monel arsenates.

(U)The product was characterized by the same methods used to establish the structure and composition of  $\text{NF}_4\text{SbF}_6$ . These were hydrolysis, elemental analysis of the hydrolysate, and nmr spectra. This information, as well as other data pertaining to  $\text{NF}_4\text{AsF}_6$  and  $\text{NF}_4\text{SbF}_6$ , is given in a recent publication.<sup>1</sup>

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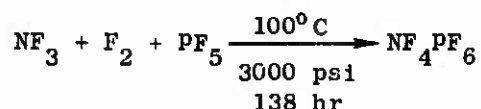
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(U)We have found that extractions with liquid HF lead to no improvement in purity of  $\text{NF}_4\text{AsF}_6$ . Thus it appears that while  $\text{NF}_4\text{AsF}_6$  is about half as soluble in HF as is  $\text{NF}_4\text{SbF}_6$ , the Monel-arsenate impurities are more soluble than the Monel antimonates. As a result of our inability to purify the  $\text{NF}_4\text{AsF}_6$ , we have found little use for it except in one experiment that will be described later.

(U)The rate of formation of  $\text{NF}_4\text{AsF}_6$  was deduced from the 17% of  $\text{NF}_3$  converted into solid in ten days of reaction at  $125^\circ\text{C}$ . Under similar conditions of temperature and pressure and in two days, a 22% conversion of  $\text{NF}_3$  into  $\text{NF}_4^+$  antimonates was observed. Thus the rate of formation of  $\text{NF}_4\text{AsF}_6$  is at least a factor of five slower.

### 3. (C) $\text{NF}_4\text{PF}_6$

(C)The salt  $\text{NF}_4\text{PF}_6$  was synthesized by the reaction:



On completion of the heating period, the residual starting materials were removed from the reactor and measured. From our experience in previous reactions of this type, we expected some fluorine would have reacted with the Monel vessel to form more fluoride than already present from the passivation procedure. We also expected the Lewis acid, in this case  $\text{PF}_5$ , to react with the fluorides to form Monel- $\text{PF}_6^-$  salts. Thus the only reliable index to the extent of  $\text{NF}_4^+$  salt formation was the consumption of  $\text{NF}_3$ . Approximately 1.6% less  $\text{NF}_3$  was recovered than was originally present. This indicated the possible presence of about 0.4 g of  $\text{NF}_4\text{PF}_6$ . When the reactor was cut open, a thin layer of product was observed uniformly distributed on the inner surface. Some of the product was hydrolyzed and yielded  $\text{NF}_3$  and  $\text{O}_2$ , as expected from  $\text{NF}_4\text{PF}_6$ .

(C)The rate of this reaction was a factor of at least 50 slower than the antimonate reaction. The rate implied that it would be necessary to heat the reaction mixture for about 50 days to prepare sufficient compound with which to undertake complete characterization.

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## 4. (C) NF<sub>4</sub>BF<sub>4</sub>

(C) From the results on the syntheses of NF<sub>4</sub>PF<sub>6</sub>, it was expected that the formation of NF<sub>4</sub>BF<sub>4</sub> by direct synthesis would be extremely slow. It was also expected that NF<sub>4</sub>BF<sub>4</sub> might be much less thermally stable than the NF<sub>4</sub><sup>+</sup> salts having larger anions. Thus the synthesis might be adversely affected by too high a reaction temperature. As a result we chose to heat the reaction mixture at 100°C. The reaction was carried out for 185 hours at an initial reactant pressure of 3000 psi.

(C) Isolation and analysis of residual starting materials indicated that as much as 0.7 g of product might be present. However, later observations showed that this could not be true. We used the apparent consumption of NF<sub>3</sub> as an indicator of the extent of NF<sub>4</sub><sup>+</sup> salt formation. BF<sub>3</sub> was separated from NF<sub>3</sub> by absorbing BF<sub>3</sub> in aqueous base. This procedure evidently resulted in hydrolysis of some NF<sub>3</sub>, leading to an incorrect determination of NF<sub>4</sub><sup>+</sup> salt present.

(C) After residual starting materials had been removed, the reactor was cut open and a small quantity of solid was scraped out. We chose to employ thermal decomposition as the method of characterization. In this case, we expected that heating the isolated solids would result in evolution of NF<sub>3</sub>, F<sub>2</sub>, and BF<sub>3</sub> if NF<sub>4</sub>BF<sub>4</sub> were present. A portion of the isolated solids was heated slowly to above 300°C in an evacuated vessel that had been passivated with fluorine. Only a few millimeters of gas were evolved. The gas contained F<sub>2</sub>, NF<sub>3</sub>, and SiF<sub>4</sub>, but no BF<sub>3</sub> was observed. The small amount of BF<sub>3</sub> to be expected from the thermal decomposition could have been absorbed by Monel metal fluorides. This conclusion was based on the fact that in a separate observation, BF<sub>3</sub> was absorbed by a passivated copper surface but none of the SiF<sub>4</sub> present in the BF<sub>3</sub> was removed. Nevertheless, the above experiment was inconclusive with respect to the direct synthesis of NF<sub>4</sub>BF<sub>4</sub> but lent substance to the hypothesis that the rate of formation of NF<sub>4</sub><sup>+</sup> salts in these direct synthesis reactions is strongly influenced by the acidity of the Lewis acid involved.

(C) The presence of SiF<sub>4</sub> in the gases evolved during thermal decomposition, along with the presence of both NF<sub>3</sub> and F<sub>2</sub>, can be explained if the salt

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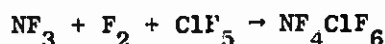
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( $\text{NF}_4$ ) $_2\text{SiF}_6$  was present. This seems very unlikely in view of the relative acidity of  $\text{SiF}_4$  in HF. The  $\text{SiF}_4$  arose from reaction of  $\text{F}_2$  with the silicon present in Monel metal.

(C) In a later experiment, a mixture of  $\text{NF}_3$ ,  $\text{F}_2$ , and  $\text{BF}_3$  was heated at  $150^\circ\text{C}$  and high pressure for three weeks. (The decomposition of  $\text{NF}_4\text{BF}_4$  is detectable in a mass spectrometer experiment at  $176^\circ\text{C}$ ,<sup>2</sup> thus  $150^\circ\text{C}$  was selected as the reaction temperature.) On completion of the heating period, the reactor was evacuated, weighed and heated to  $300^\circ\text{C}$ . The system was passivated with respect to  $\text{BF}_3$ . The reactor lost 4 mg and the gas evolved contained  $\text{NF}_3$ ,  $\text{BF}_3$ ,  $\text{CF}_4$ , and possibly a trace of  $\text{F}_2$ . There were no more than 4 mg of  $\text{NF}_4\text{BF}_4$  formed in this experiment. However, the synthesis of  $\text{NF}_4\text{BF}_4$  has been accomplished by means of a metathesis reaction that will be described in a later section of this report.

## 5. (C) Attempted Direct Synthesis of $\text{NF}_4\text{ClF}_4$ and $\text{NF}_4\text{ClF}_6$

(C) From experience with the weaker Lewis acids  $\text{PF}_5$  and  $\text{BF}_3$ , it seemed unlikely that  $\text{ClF}_3$  and  $\text{ClF}_5$  would form the hypothetical salts  $\text{NF}_4\text{ClF}_4$  and  $\text{NF}_4\text{ClF}_6$  in direct synthesis reactions of the following type:



These reactions were, however, attempted. In the first of these, the  $\text{F}_2$  and  $\text{ClF}_3$  combined to form the equilibrium concentration of  $\text{ClF}_5$ . Thus, the study of the mixture of  $\text{NF}_3$ ,  $\text{F}_2$ , and  $\text{ClF}_3$  was essentially the study of both of the hypothetical reactions.

(C) The mixture was heated at  $100^\circ\text{C}$  and 3000 psi initial pressure for 65 hours. The reaction vessel was passivated first with respect to fluorine and next with respect to  $\text{SbF}_5$  to avoid possible reactions of the interhalogens with metal fluorides. Unfortunately, our analysis

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of reaction products later showed that excess  $\text{SbF}_5$  was present in the vessel and that it had reacted to form  $\text{NF}_4^+$  antimonate salts.

On completion of reaction, the starting materials were removed and the presence of  $\text{NF}_3$ ,  $\text{F}_2$ ,  $\text{ClF}_3$ , and  $\text{ClF}_5$  was confirmed. The evacuated vessel was then heated slowly up to  $350^\circ\text{C}$  and the pressure of evolved gas was observed. Above  $225^\circ\text{C}$  the pressure rose from several millimeters to about one atmosphere. The gas contained  $\text{NF}_3$ ,  $\text{F}_2$ ,  $\text{SiF}_4$ , and about 2%  $\text{ClF}_5$ . At first, we attributed the presence of  $\text{ClF}_5$  to the decomposition of the hypothetical salt  $\text{NF}_4\text{ClF}_6$ , but later experiments in which we heated mixtures of  $\text{NF}_3$ ,  $\text{F}_2$ , and  $\text{ClF}_5$  in vessels having no  $\text{SbF}_5$  present showed that no  $\text{ClF}_5$  was evolved on thermal decomposition. Thus, the  $\text{ClF}_5$  found in the gas from the first experiment was due to an interaction with  $\text{SbF}_5$ . This interaction could have been



However, a separate study of this mixture indicated the occurrence of a complicated reaction system that gave no clear-cut evidence for the formation of the  $\text{ClF}_6^+$  cation. The interaction of  $\text{ClF}_5$  and  $\text{SbF}_5$  could also have been simply the formation of the well-known complex formed by these two reagents and its thermal decomposition above  $300^\circ\text{C}$  to yield an observable amount of  $\text{ClF}_5$ . It is necessary to assume that the similar complex formed by  $\text{ClF}_3$  and  $\text{SbF}_5$  did not decompose in the temperature range studied, since no  $\text{ClF}_3$  was found in the products of thermal decomposition. Because later experiments provided no evidence for evolution of either  $\text{ClF}_3$  or  $\text{ClF}_5$  on thermal decomposition, it is necessary to conclude, as expected, that no  $\text{NF}_4\text{ClF}_4$  nor  $\text{NF}_4\text{ClF}_6$  had been formed by the direct synthesis route.

## 6. (C) $\text{NF}_4\text{PtF}_6$

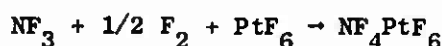
(C)The systems  $\text{NF}_3/\text{PtF}_6$  and  $\text{NF}_3/\text{F}_2/\text{PtF}_6$  were tested for interactions that might form solid salts. A vessel containing solid and about 90 mm of gaseous  $\text{PtF}_6$  as well as  $\text{NF}_3$  at about 1250 psi was allowed to stand for 137 hours at room temperature. Since all the  $\text{NF}_3$  originally present could be recovered from the reaction vessel, it was clear that no interaction occurred at room temperature. The system was not studied at higher temperatures.

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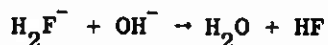
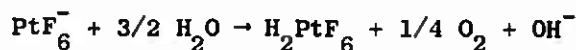
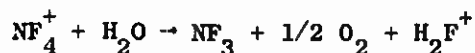
(C) The system  $\text{NF}_3/\text{F}_2/\text{PtF}_6$  was examined at three temperatures. There was no reaction at 2000 psi and after 143 hours at room temperature; there was little if any reaction after 400 hours at  $50^\circ\text{C}$ . The mixture was then heated at  $125^\circ\text{C}$  for 1700 hours, during which time all of the  $\text{PtF}_6$  present reacted to form a solid product. Since this reaction was not monitored closely, the rate of reaction could not be determined, and it is possible that the reaction was complete in a much shorter time.

(C) The mixture that formed the solid product contained 214 mmole of  $\text{NF}_3$ , 132 mmole of  $\text{F}_2$ , and 45 mmole of  $\text{PtF}_6$ . The consumption of the three components was consistent with the reaction:



The  $\text{F}^{19}$  nmr spectrum was obtained on a dilute solution of the salt in liquid HF. The NF triplet characteristic of  $\text{NF}_4^+$  was observed at  $-214.3$  ppm from  $\text{FCCl}_3$ . This chemical shift is identical within experimental error to that observed for  $\text{NF}_4^+\text{SbF}_6^-$  and  $\text{NF}_4^+\text{AsF}_6^-$ . There was no line or lines between the positions of HF and  $\text{F}_2$  that could be attributed to  $\text{PtF}_6^-$ . The HF line was sharp; the sharpness indicated that very little fluoride exchange was occurring.

(C) Hydrolysis of the salt was consistent with the reactions:



In addition, the presence of an insoluble precipitate in the hydrolysate indicated that some hydrated  $\text{PtO}_2$  had formed in accord with reported observations on the hydrolysis of  $\text{O}_2\text{PtF}_6$ .<sup>3</sup>

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(C)Elemental analysis was in reasonably good agreement with a product composition of  $\text{NF}_4\text{PtF}_6$  contaminated with  $\text{Ni}(\text{PtF}_6)_2$  from the nickel reactor:

	Calc	Found
N	3.51	3.40
F	48.88	45.27
Pt	47.61	45.58
Ni	-0-	0.88

(C)The infrared spectrum was obtained from a sample of the product dispersed in KCl and pressed into a transparent pellet. The spectrum contained the intense line of  $\text{NF}_4^+$  at  $1155\text{ cm}^{-1}$  and the  $\text{PtF}_6^-$  absorption<sup>4</sup> at  $647\text{ cm}^{-1}$ .

(C)During preparation of the nmr sample, it was observed that most of the sample of the impure  $\text{NF}_4\text{PtF}_6$  had dissolved in HF while a small amount of insoluble material appeared in the bottom of the Kel-F tube. By analogy with impure  $\text{NF}_4\text{SbF}_6$ , in which the impurities are only slightly soluble in HF, it seemed possible that the  $\text{NF}_4\text{PtF}_6$  could be purified by extraction in HF. The attempted purification was carried out in an apparatus developed for use in metathetical reactions. The apparatus consists of two Kel-F tubes joined to a common fitting through flexible FEP Teflon lines. The common fitting is also connected to a valve and through the valve to the vacuum system. One of the Kel-F tubes is fitted with a filter having a fine grade of Zitex Kel-F/Teflon filter paper. Insoluble material can be separated by pouring the solution through the filter and through the flexible line to the second vessel.

(C)During the attempted purification, the Kel-F tubes formed deep stress cracks and began to leak HF vapor. The separation was completed and the HF removed as rapidly as possible. Before the vessels failed, however, we obtained a very approximate value for the solubility of  $\text{NF}_4\text{PtF}_6$  in HF. This was about 0.5 g/ml of HF. We also noted that the color of the insoluble residue differed from that of the crude  $\text{NF}_4\text{PtF}_6$  and from the presumably purified material. We concluded that a separation of impurities had been accomplished.

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(C) Stress cracking of Kel-F has occurred on several occasions, and the only factor common to all vessel failures seems to be length of time in use. During use, the vessels are generally cooled many times to liquid nitrogen temperature and warmed to room temperature with a hot air gun. Quite possibly, this temperature cycling is the major cause of stress cracking. We have not been able to show that any chemical or chemical mixture is the cause. In view of the above, we concluded that crude  $\text{NF}_4\text{PtF}_6$  could be purified in a new Kel-F/Teflon apparatus.

## B. Metathesis Reactions

(C) It was obvious that the synthesis of many possibly interesting  $\text{NF}_4^+$  salts, especially those containing oxyanions, would not be possible under the conditions of the temperature/pressure activated reactions. Consequently, we sought to find the proper reagents and conditions for metathesis reactions. The problem was clearly one of obtaining starting reagents that were soluble in the solvent of choice and that would form double decomposition products whose solubilities differed substantially. We have found a number of such systems.

(C) The solvent of choice was liquid HF, in which  $\text{NF}_4^+$  salts are quite soluble and which does not react with them. The solubilities of a number of inorganic compounds in HF are given by Simons.<sup>5</sup> Solubility data on a number of metal fluorides<sup>6</sup> and on two alkali metal hexafluoroantimonates<sup>7,8</sup> were also available. From these data, it seemed clear that the  $\text{SbF}_6^-$  anion could be removed from solution by precipitating it as a relatively insoluble alkali metal salt. The solubility behavior of the new  $\text{NF}_4^+$  salt formed on metathesis could only be estimated. For this estimation, we used the hypothesis that the  $\text{NF}_4^+$  ion could be treated as though it were an extension of the alkali metal ions,  $\text{NF}_4^+$  being much larger than  $\text{Cs}^+$ . Thus, the alkali metal fluorides which increase in solubility and in size from LiF through CsF could be used as an indicator for the solubility of the hypothetical salt  $\text{NF}_4^+\text{F}^-$ . In HF, the fluoride ion would necessarily be present in the solvated form. These considerations suggested that the desired product of the metathesis reaction, the  $\text{NF}_4^+$  salt, would be

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present in solution, while the co-product of metathesis, for example,  $\text{LiSbF}_6$ , would be present as a precipitate.

(C) These conclusions were proved correct. However, the solubilities of the alkali metal fluorides are the only ones we have studied that follow the correlation of increased solubility with larger size. Other alkali metal salts show either a minimum or a maximum solubility of the potassium salt, and the solubility of the  $\text{NF}_4^+$  salt cannot be estimated by this qualitative extrapolation. Fortunately, all  $\text{NF}_4^+$  salts are quite soluble and are reasonably separable from the insoluble products of metathesis.

## 1. (C) $\text{NF}_4\text{HF}_2$

(C) The first metathesis reaction studied was that of  $\text{NF}_4\text{SbF}_6$  with  $\text{LiF}$  as follows:



The reaction was carried out in the apparatus shown in Fig. 1. Six mmole of the reactants were placed in separate vessels. This operation was carried out in a drybox to avoid reaction of the  $\text{NF}_4^+$  salt with water vapor and to avoid introducing water as a contaminant in the reaction. The apparatus was then connected to the vacuum line and about 2.5 cc of HF was condensed into each tube. The nearly saturated solution of  $\text{LiF}$  was poured into the vessel containing the  $\text{NF}_4\text{SbF}_6$  in HF. A white precipitate formed immediately. This was later shown to be  $\text{LiSbF}_6$  from its X-ray powder pattern.

(C) About 2.5 cc of HF was removed from the mixture to concentrate the  $\text{NF}_4^+$  salt and to precipitate additional  $\text{LiSbF}_6$ . Part of the solution remaining was decanted into a Kel-F nmr tube and part into the empty tube from which the  $\text{LiF}$  solution had been removed.

(C) The nmr tube was sealed off and an nmr spectrum of the contents was obtained. The  $\text{NF}_4^+$  triplet was present at very substantial intensity. No  $\text{SbF}_6^-$  line was detectable, while the HF line was shifted downfield a few ppm from its normal position. This shift was taken to indicate

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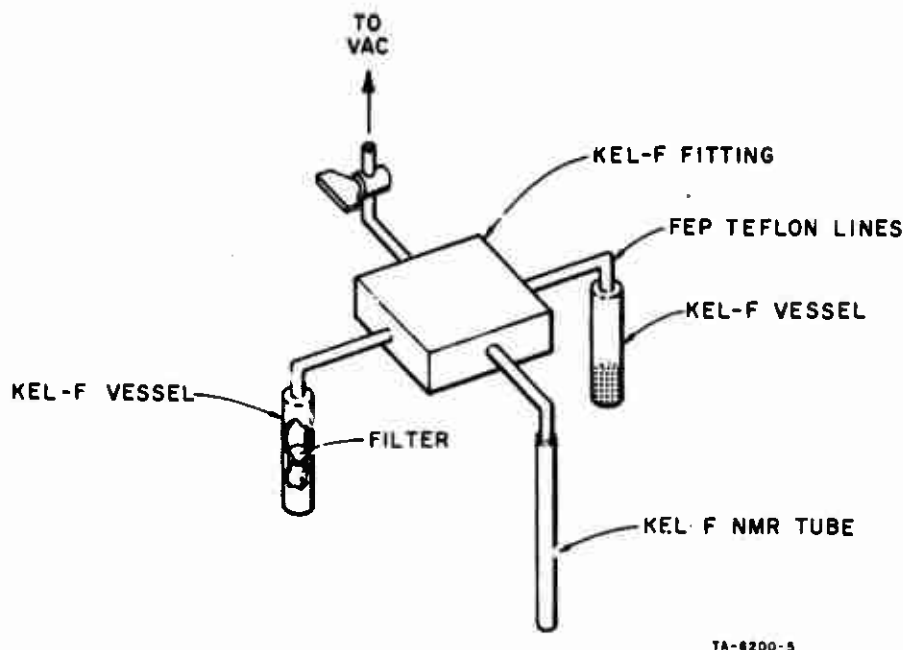


FIG. 1 METATHESIS REACTION APPARATUS

fluoride ion exchange with HF as might be expected from the presence of  $\text{HF}_2^-$ . Subsequent nmr spectra taken over a period of three weeks showed no change in the concentration of  $\text{NF}_4^+$ , indicating that the salt was stable in HF solution.

(C)The solvent remaining in solution in the metathesis apparatus was removed at room temperature. A white solid was isolated that was initially thought to be the expected product  $\text{NF}_4\text{HF}_2$ . Later, however, the white solid was shown to be the fraction of  $\text{LiSbF}_6$  that is soluble in HF. All attempts to isolate  $\text{NF}_4\text{HF}_2$  resulted in decomposition of the salt into  $\text{NF}_3$ ,  $\text{F}_2$ , and HF at temperatures of  $-44^\circ\text{C}$  and above.

(C)Solvent could be removed at  $-78^\circ\text{C}$  only very slowly. After a week of pumping on the solution at this temperature, there remained a product that had the appearance of a wet solid. When the product was warmed to  $-44^\circ\text{C}$ ,  $\text{NF}_3$ ,  $\text{F}_2$ , and HF were evolved. The quantity of  $\text{NF}_3$  evolved was almost equivalent to the amount of  $\text{NF}_4^+$  originally present. Thus  $\text{NF}_4\text{HF}_2$

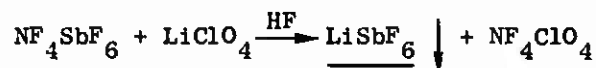
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was found to be unstable at  $-44^{\circ}\text{C}$  and above. The instability of the bifluoride was taken to indicate that the fluoride, if a system could be found in which to synthesize it, would also be unstable.

## 2. (C) $\text{NF}_4\text{ClO}_4$

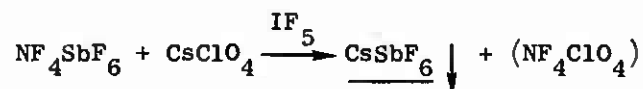
(C)The salt  $\text{NF}_4\text{ClO}_4$  was synthesized in the reaction:



The reaction was carried out in the metathesis apparatus and the HF solution of  $\text{NF}_4\text{ClO}_4$  was isolated as described above. During removal of solvent at room temperature, it immediately became obvious that the salt was decomposing by evolution of gas. The first sample of gas taken for infrared analysis contained only  $\text{NF}_3$  and HF. Later, however, the gas contained both  $\text{NF}_3$  and  $\text{FClO}_4$  as would be expected from the decomposition of  $\text{NF}_4\text{ClO}_4$ . When decomposition was complete and the evolved gases and solvent were removed, the weight loss was equal to that expected for the complete decomposition of  $\text{NF}_4\text{ClO}_4$  into  $\text{NF}_3$  and  $\text{FClO}_4$ .

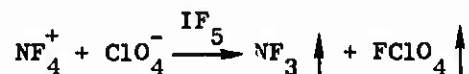
(C)In subsequent experiments we showed that  $\text{NF}_4\text{ClO}_4$  was stable up to  $-27.5^{\circ}\text{C}$ , but that above this temperature it decomposed as given above.

(C)It was thought at first that the decomposition might be catalyzed by the small amount of HF undoubtedly still present in the solid  $\text{NF}_4\text{ClO}_4$  isolated at reduced temperatures. The preparation of  $\text{NF}_4\text{ClO}_4$  in a solvent other than HF could verify this. We selected  $\text{IF}_5$  as the solvent, determined compatibility and solubility of  $\text{NF}_4\text{SbF}_6$  and some perchlorates in  $\text{IF}_5$ , and carried out the reaction. It should be noted that  $\text{LiClO}_4$  reacts in  $\text{IF}_5$  to form  $\text{FClO}_3$  among other products, while  $\text{CsClO}_4$  is unreactive and reasonably soluble. (A later section of this report contains a summary of solubility studies carried out in support of work on metathesis reactions in HF,  $\text{BrF}_5$ , and  $\text{IF}_5$ .) Thus, the reaction carried out was:

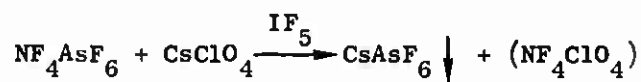


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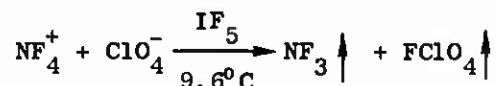
However, the product decomposed as soon as the  $\text{IF}_5$  melted at about  $9.6^\circ\text{C}$ . The reaction was:



(C) It was reported by workers at Stauffer<sup>9</sup> that  $\text{NF}_4\text{AsF}_6$  and  $\text{CsClO}_4$  were stable in  $\text{IF}_5$  at room temperature. In view of the above results on  $\text{NF}_4\text{SbF}_6$  and  $\text{CsClO}_4$  in  $\text{IF}_5$ , we carried out the similar experiment:



and the result was:



These reactions were carried out both in quartz and in Kel-F vessels. The results were not affected by the type of vessel used. The  $\text{IF}_5$  used in these studies was water white. This material was obtained only after extensive passivation of the reaction system and vacuum lines with  $\text{IF}_5$  and  $\text{F}_2$ . The  $\text{IF}_5$  was stored in a large Kel-F vessel containing finely divided KF and a magnetic stirring bar; the KF was present to remove HF.  $\text{IF}_5$  transferred from the cylinder to the storage receiver was usually colored a light yellow-red. The color disappeared on addition of fluorine.  $\text{IF}_5$  purified by treatment with KF and  $\text{F}_2$  did not react with either  $\text{NF}_4\text{SbF}_6$  or  $\text{NF}_4\text{AsF}_6$ , the weight of sample being unchanged on addition and subsequent removal of solvent.

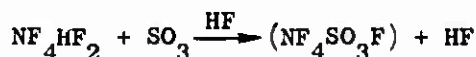
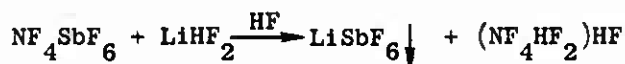
(C) From the evidence we have obtained on metathesis in HF and on the reactions of  $\text{NF}_4\text{SbF}_6$  and  $\text{NF}_4\text{AsF}_6$  with  $\text{CsClO}_4$  in purified  $\text{IF}_5$ , it seems clear that  $\text{NF}_4\text{ClO}_4$  is intrinsically unstable at temperatures above  $-27.5^\circ\text{C}$ . This conclusion is based on strong evidence and clearly contradicts the report of the Stauffer workers.

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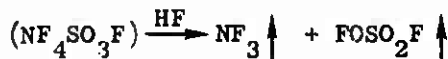
(C) In one experiment, we tested the sensitivity of  $\text{NF}_4\text{ClO}_4$  by striking it repeatedly with a hammer on a steel plate cooled to  $-35^\circ\text{C}$ . There was no evidence of sensitivity. Both  $\text{NF}_4\text{SbF}_6$  and  $\text{NF}_4\text{AsF}_6$  are also insensitive in this test carried out at room temperature. Unfortunately, the observed instability of  $\text{NF}_4\text{ClO}_4$  makes it of little use as a solid oxidizer.

### 3. (C) Attempted Preparation of $\text{NF}_4\text{SO}_3\text{F}$

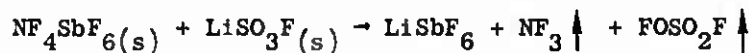
(C) We attempted preparation of  $\text{NF}_4\text{SO}_3\text{F}$  in the following set of reactions:



However, the reaction



occurred rapidly at room temperature and slowly at  $-78^\circ\text{C}$ . In addition, the reaction:



occurred at room temperature. Thus the salt  $\text{NF}_4\text{SO}_3\text{F}$  is unstable at  $-78^\circ\text{C}$  and is probably unstable at lower temperatures.

### 4. (C) Attempted Preparation of $\text{NF}_4\text{NO}_3$

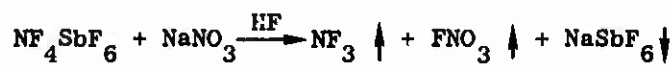
(C) Because  $\text{NF}_4\text{ClO}_4$  was unstable, it seemed quite likely that the corresponding nitrate would also be unstable. Nevertheless, experiments were carried out to determine whether  $\text{NF}_4\text{NO}_3$  could be made. The interaction of nitrate with anhydrous HF is complex<sup>5</sup> and there is some question<sup>8</sup> concerning the species actually present. The reaction of nitrate with HF may involve protonation to form  $\text{HONO}_2$  or  $\text{H}_2\text{NO}_3^+$  or it might involve formation of  $\text{H}_3\text{O}^+$ ,  $\text{NO}_2^+$ , and  $\text{HF}_2^-$ . It is also possible that an equilibrium exists that involves all these species.

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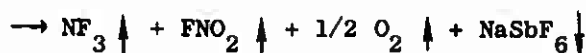
(C) Our results on dissolving  $\text{NF}_4\text{SbF}_6$  and  $\text{NaNO}_3$  in HF at room temperature indicated that the species formed from nitrate in HF were probably not simply the protonated ones. The attempted reaction was:



On separation of  $\text{NaSbF}_6$  and removal of HF, the desired  $\text{NF}_4\text{NO}_3$  could be recovered if the system were stable. Instead, the HF solution evolved  $\text{NF}_3$  steadily at room temperature. When the evolution of gas ceased and the solvent was removed, the observed weight loss was that to be expected from

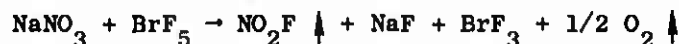


or



However, we observed none of the NOF compounds; only  $\text{NF}_3$  and some non-condensable gas were present. Our results could be explained if  $\text{FNO}_2$  were present in the form  $\text{NO}_2^+$  and  $\text{HF}_2^-$ . On evaporation of solvent, the  $\text{FNO}_2$  would also be removed, thus accounting for the observed weight loss. Whether  $\text{FNO}_2$  was present in the HF was not determined because it was obvious that  $\text{NF}_4\text{NO}_3$  could not be prepared in this system.

(C) We also explored the possibility that  $\text{NF}_4\text{NO}_3$  could be formed in a metathesis reaction in a solvent other than HF, in this case  $\text{BrF}_5$ .  $\text{BrF}_5$  is an adequate solvent for  $\text{NF}_4\text{SbF}_6$ , but when  $\text{BrF}_5$  was placed in contact with sodium or cesium nitrates, the following reaction occurred:



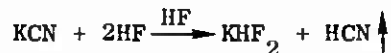
This reaction along with the reaction in HF rules out the possibility of forming  $\text{NF}_4\text{NO}_3$ .

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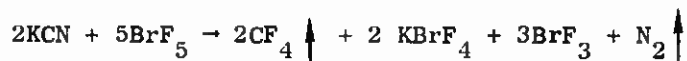
(C)To obtain some information on the possible stability of  $\text{NF}_4\text{NO}_3$ , we studied the interaction of the two solids  $\text{NaNO}_3$  and  $\text{NF}_4\text{SbF}_6$  in the temperature range from room temperature to  $215^\circ\text{C}$ . If the two finely divided and well mixed solids react at room temperature or even at some moderately elevated temperature, it is most probable that the  $\text{NF}_4^+$  salt derivable by means of double decomposition in solution will be unstable. On the other hand, if the two solids react only at some elevated temperature, it is possible to conclude only that the  $\text{NF}_4^+$  salt derivable on metathesis might be stable. Thus, on examining the solid/solid interaction of  $\text{NaNO}_3$  and  $\text{NF}_4\text{SbF}_6$ , we found that the two solids gave off  $\text{NF}_3$  and noncondensables very slowly at room temperature and evolved  $\text{NF}_3$  and  $\text{NO}_2$  plus noncondensables also very slowly up to  $215^\circ\text{C}$ . From this we concluded that  $\text{NF}_4\text{NO}_3$ , if formed, would very probably be unstable.

## 5. (C) Observations on $\text{CN}^-$

(C)In view of the reaction:



we concluded that it would not be possible to carry out the synthesis of  $\text{NF}_4\text{CN}$  in HF. We thought it might be possible to carry out the synthesis in  $\text{BrF}_5$ . It soon became apparent, however, that KCN was unstable in  $\text{BrF}_5$  and reacted as follows:



(C)The solid/solid reaction of KCN and  $\text{NF}_4\text{SbF}_6$  was also studied from 25 to  $110^\circ\text{C}$ . The mixture continuously but slowly evolved gas. At  $110^\circ\text{C}$ , the reaction rate increased appreciably and gave off  $\text{NF}_3$ ,  $\text{CF}_4$ , and noncondensables. We concluded that even if  $\text{NF}_4\text{CN}$  could be synthesized, it would probably be unstable.

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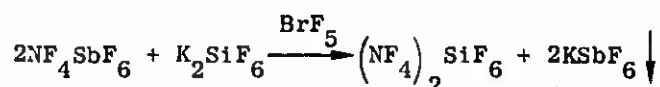
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## 6. (C) Observations on $\text{SiF}_6^-$

(C) Analogous to the cyanides, the hexafluorosilicates also decompose in HF, i.e.:



Consequently, we attempted the synthesis of  $(\text{NF}_4)_2\text{SiF}_6$  by the reaction:



It was first determined that the starting reagents were soluble in  $\text{BrF}_5$  while  $\text{KSbF}_6$  was relatively insoluble. We expected that  $(\text{NF}_4)_2\text{SiF}_6$  would be quite soluble in view of the generally high solubility of  $\text{NF}_4^+$  salts in the solvents we have studied.

(C) When these reagents were dissolved in  $\text{BrF}_5$ , no  $\text{KSbF}_6$  was formed. We also observed that there was no adverse decomposition of the starting materials. The latter indicates that the hypothetical salt  $(\text{NF}_4)_2\text{SiF}_6$  will probably be stable, but the fact that no  $\text{KSbF}_6$  was formed showed that no reaction occurred to form the desired products. The lack of reaction was surprising in view of the solubility relationships which were ideal for the occurrence of a metathesis reaction. We can understand the lack of reaction if one or both of the starting materials dissolved without dissociation into ionic species. We are currently studying other solvents, including  $\text{BrF}_3$  and  $\text{IF}_5$ , in which a metathesis reaction might possibly occur.

## 7. (U) Preparation of Tetrafluorochlorate and Hexafluorobromate Salts

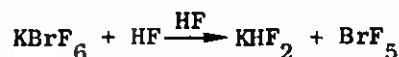
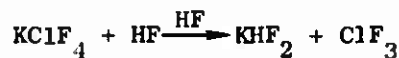
Among the energetic anions with which it might be possible to associate the  $\text{NF}_4^+$  cation in a stable compound are  $\text{ClF}_4^-$ ,  $\text{BrF}_4^-$ , and  $\text{BrF}_6^-$ .  $\text{KBrF}_4$  forms readily from  $\text{KF}$  and  $\text{BrF}_3$  at room temperature,<sup>10</sup> while other

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metal salts of this anion have not been well defined and some lose  $\text{BrF}_3$  at ordinary temperatures. Certain alkali metal ( $\text{K}^+$ ,  $\text{Rb}^+$ , and  $\text{Ca}^+$ ) salts of  $\text{ClF}_4^-$  and  $\text{BrF}_6^-$  have been synthesized and are reportedly quite stable.<sup>11</sup> We have prepared the potassium and cesium salts of these anions by modifying the method of Whitney et al., who reported only partial conversion of the alkali metal fluorides to the complexes at  $100^\circ\text{C}$  and a reaction time of one hour.<sup>11</sup> Increased reaction time and improved stirring yielded 97% conversions. We later found that the reaction also occurs at room temperature. The conversion was about 16 to 19% in one to two hours.

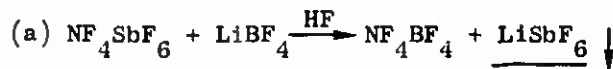
(C) We have tested the alkali metal  $\text{ClF}_4^-$  and  $\text{BrF}_6^-$  salts in HF. The reactions



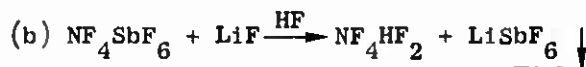
occur slowly at room temperature. These reactions rule out the use of HF as a solvent, and we have carried out some experiments to determine whether  $\text{BrF}_5$  and  $\text{IF}_5$  are suitable solvents for these salts. The solubilities of these salts are given in Section D of this report. The cesium salts are sufficiently soluble to show whether a metathesis reaction can occur with  $\text{NF}_4\text{SbF}_6$  in  $\text{BrF}_5$  and will permit us to show whether the  $\text{NF}_4^+$ /interhalogen anion salts can be prepared and are stable.

## C. (C) Preparation of Purified $\text{NF}_4\text{BF}_4$

(C) The preparation of  $\text{NF}_4\text{BF}_4$  has been achieved by carrying out metathetical reactions in liquid HF:



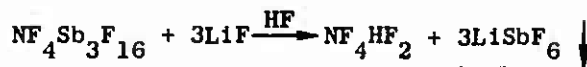
and



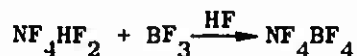
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or



followed by



(C)The purity of the  $\text{NF}_4\text{BF}_4$  that is obtained is limited by the dissolved  $\text{LiSbF}_6$  that accompanies the  $\text{NF}_4\text{BF}_4$  or  $\text{NF}_4\text{HF}_2$  on filtration.

(C)The solubilities of Li, Na, K, Rb, and Cs tetrafluoroborates in liquid HF were determined to be 5.27, 3.14, 0.76, 2.2, and 9.2 molar, respectively. If  $\text{NF}_4^+$  behaves in solution as an alkali metal ion larger than  $\text{Cs}^+$ ,  $\text{NF}_4\text{BF}_4$  should be more soluble than  $\text{CsBF}_4$ . Assuming that  $\text{NF}_4\text{BF}_4$  is as soluble as  $\text{CsBF}_4$  and using the solubility of  $\text{LiSbF}_6$  in HF (0.22 molar), calculations showed that  $\text{NF}_4\text{BF}_4$  with a maximum of 97% purity might be obtained. Since  $\text{NF}_4\text{HF}_2$  is probably more soluble than  $\text{NF}_4\text{BF}_4$ , somewhat higher purities should be obtained when a saturated  $\text{NF}_4\text{HF}_2$  solution is filtered.

(C)Actual purity of the  $\text{NF}_4\text{BF}_4$  obtained in these metathesis reactions in HF was never higher than 88%, with the major impurity being  $\text{LiSbF}_6$ , as expected. The large difference between the calculated and the actual purity is probably the increased solubility of  $\text{LiSbF}_6$  due to the high ionic strength in the concentrated solutions. Another possible source of impurity is finely divided solid  $\text{LiSbF}_6$  passing through the medium-porosity Teflon filter paper.

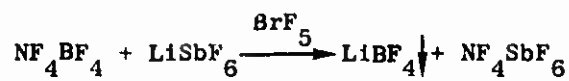
(C)Since  $\text{NF}_4\text{SbF}_6$  and  $\text{NF}_4\text{AsF}_6$  are soluble in liquid  $\text{HF}$ ,  $\text{NF}_4\text{BF}_4$  was also expected to have an appreciable solubility.  $\text{LiF}$  has a solubility of less than 1.25 mg/g of  $\text{BrF}_5$ . Thus it appeared that extraction of the  $\text{NF}_4\text{BF}_4$ - $\text{LiSbF}_6$  mixture should yield pure  $\text{NF}_4\text{BF}_4$ .

(C)When a sample consisting of  $\text{NF}_4\text{BF}_4$  and  $\text{LiSbF}_6$  was treated with  $\text{BrF}_5$ , the soluble fraction contained very little lithium. The antimony content, however, was almost the same as in the original sample, the overall  $\text{NF}_4^+$  content indicated a mixture of  $\text{NF}_4\text{BF}_4$  and  $\text{NF}_4\text{SbF}_6$ . Another sample,

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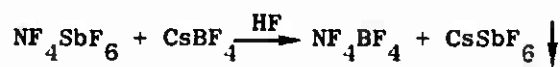
prepared using excess  $\text{LiF}$  and thus consisting of a mixture of  $\text{NF}_4\text{BF}_4$ ,  $\text{LiSbF}_6$ , and  $\text{LiBF}_4$ , was treated with three successive portions of  $\text{BrF}_5$ .  $\text{LiBF}_4$  is insoluble in  $\text{BrF}_5$  and should filter out with the  $\text{LiSbF}_6$ . Analyses again indicated that the soluble fractions were mixtures of  $\text{NF}_4\text{BF}_4$  and  $\text{NF}_4\text{SbF}_6$ . The antimony content was almost the same in each fraction.

(C) Thus it appears that the following reaction occurred:



This reaction must occur as the material dissolves, since the antimony is not preferentially dissolved. The  $\text{NF}_4^+$  may be removed from the lattice with the closest  $\text{SbF}_6^-$  or  $\text{BF}_4^-$ , leaving behind the insoluble  $\text{LiBF}_4$  or  $\text{LiSbF}_6$ .

(C) Since  $\text{CsSbF}_6$  was found to have a lower molar solubility in  $\text{HF}$  than  $\text{LiSbF}_6$ , treatment of the  $\text{NF}_4\text{SbF}_6$ - $\text{NF}_4\text{BF}_4$  mixture with  $\text{CsBF}_4$  in  $\text{HF}$  should convert much of the  $\text{NF}_4\text{SbF}_6$  into  $\text{CsSbF}_6$ :



The soluble fraction, after filtering, should contain less  $\text{SbF}_6^-$  than the product after the  $\text{LiBF}_4$  reaction, and the exchange of  $\text{SbF}_6^-$  in  $\text{BrF}_5$  might not occur with  $\text{CsSbF}_6$ .  $\text{CsSbF}_6$  and  $\text{CsBF}_4$  are insoluble in  $\text{BrF}_5$  and will filter out. The  $\text{NF}_4\text{SbF}_6$ - $\text{NF}_4\text{BF}_4$  mixture was therefore treated with excess  $\text{CsBF}_4$  in  $\text{HF}$ , the saturated solution filtered, and the soluble product extracted with  $\text{BrF}_5$ . The purity of the final product was 90.2% as indicated by gas evolution on hydrolysis which was only slightly higher than the original mixture, but antimony content was only 2.13% compared with almost 10% originally. The remainder of impurity may have been finely divided  $\text{CsBF}_4$  which passed through the filter.

(C) Consequently, another metathesis reaction was carried out using  $\text{NF}_4\text{SbF}_6$  and  $\text{CsF}$ , filtering the concentrated solution, adding  $\text{BF}_3$ , and extracting the solid product with  $\text{BrF}_5$ . An extra fine porosity Teflon filter paper was used to reduce the chance of solid passing through.

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Data from hydrolysis, pyrolysis, and analysis for  $\text{Cs}^+$  indicate the sample was 92%  $\text{NF}_4\text{BF}_4$  and 8%  $\text{NF}_4\text{SoF}_6$ .

## D. (U) Solubility Studies

(U)A number of solubility studies on pertinent compounds have been carried out in support of our work on metathesis reactions. The solubility data have been used to determine whether a metathesis reaction is possible and to estimate to what extent a separation of products can be achieved.

(U)All the solids used in this study were either prepared by standard procedures or purchased, the highest commercial purity available being obtained. In addition, all the samples were thoroughly dried and then stored before use in a Vacuum Atmospheres Corp. dry box. The infrared spectra of many of the salts were obtained as an additional purity check.

(U)The same rigorous conditions were also applied to the solvents that were used. Vapor pressure and the infrared spectrum verified the purity of the particular sample.

(U)The HF solubilities of the various compounds listed in Table I were necessarily run in Kel-F vessels, while those in other solvents were determined in quartz tubes.

(U)In a typical solubility determination, the salt under study was transferred into a solubility vessel in the dry box, weighed, and then connected to the vacuum line. Enough purified solvent was added to completely dissolve the solute, which was easily visible with the aid of a strong illumination source placed behind the solubility tube. Solvent was then slowly removed with stirring to the first sign of a permanent precipitate. The vessel was then reweighed to determine the quantity of solvent present.

(U)The procedure is estimated to be accurate within 6% based on a similar determination of the solubility of KCl in  $\text{H}_2\text{O}$  using this method. However, the accuracy of the method decreases with decreasing solubility. Thus, for materials of very low solubility, the results are only indicative.

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Table I  
SOLUBILITIES OF PERTINENT COMPOUNDS

Compound	Solubility (mg/g)	Temperature (°C)	Compound	Solubility (mg/g)	Temperature (°C)	
in HF			in BrF <sub>5</sub>			
LiSbF <sub>6</sub>	56.2	27	LiSbF <sub>6</sub>	<1.25	27	
NaSbF <sub>6</sub>	108	30	KSbF <sub>6</sub>	<0.2	↓	
KsoF <sub>6</sub>	210	30	CsSbF <sub>6</sub>	8.1		
RbSbF <sub>6</sub>	87.3	30	NF <sub>4</sub> SbF <sub>6</sub>	152		
CsSbF <sub>6</sub>	55.5	30	LiBF <sub>4</sub>	<0.2		
NF <sub>4</sub> SbF <sub>6</sub>	2800	30	CsBF <sub>4</sub>	<0.45		
LiBF <sub>4</sub>	522	25	LiClO <sub>4</sub>	Rx		
NaBF <sub>4</sub>	366	27	KClO <sub>4</sub>	<3.84		
KBF <sub>4</sub>	101	26	CsClO <sub>4</sub>	<8.08		
RbBF <sub>4</sub>	402	28	AgClO <sub>4</sub>	<3.25		
CsBF <sub>4</sub>	2140	25	CsClF <sub>4</sub>	1.1		
LiClO <sub>4</sub>	857	27	KBrF <sub>6</sub>	<1.4		
KClO <sub>4</sub>	211	30	CsBrF <sub>6</sub>	8.1		
CsClO <sub>4</sub>	169	27	LiF	<1.60		
NF <sub>4</sub> AsF <sub>6</sub>	1370	26	Na <sup>+</sup>	<1.98		
LiAsF <sub>6</sub>	421	30	KF	Rx		
NF <sub>4</sub> PtF <sub>6</sub>	<549	26	CsF	Rx		
NF <sub>4</sub> BF <sub>4</sub>	~758	27	K <sub>2</sub> SiF <sub>6</sub>	>100		
in IF <sub>5</sub>			NF <sub>4</sub> AsF <sub>6</sub>	<66.5		
NF <sub>4</sub> SbF <sub>6</sub>	~450	27	NF <sub>4</sub> BF <sub>4</sub>	~76		
in IF <sub>5</sub>			in BrF <sub>3</sub>			
KSbF <sub>6</sub>	<6.28	↓	NF <sub>4</sub> SbF <sub>6</sub>	31.2	27	
CsClO <sub>4</sub>	112.9					
K <sub>2</sub> SiF <sub>6</sub>	<21.99					

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## E. Conclusions and Recommendations

(C) It is important to note that the series of salts,  $\text{NF}_4\text{SbF}_6$ ,  $\text{NF}_4\text{AsF}_6$ ,  $\text{NF}_4\text{PF}_6$ , and  $\text{NF}_4\text{BF}_4$ , has been shown to exist during this work. It is also important that these salts, as well as  $\text{NF}_4\text{PtF}_6$ , are thermally quite stable.  $\text{NF}_4\text{SbF}_6$  and  $\text{NF}_4\text{PtF}_6$  decompose rapidly under the conditions of a vacuum thermal stability test only above  $300^\circ\text{C}$ .  $\text{NF}_4\text{AsF}_6$  decomposes rapidly above  $250^\circ\text{C}$ , and  $\text{NF}_4\text{BF}_4$  decomposes rapidly above  $200^\circ\text{C}$ . The decomposition of  $\text{NF}_4\text{PF}_6$  was not studied. All of these salts except  $\text{NF}_4\text{PtF}_6$  decompose in the same manner, forming  $\text{NF}_3$ ,  $\text{F}_2$ , and the anion precursor.  $\text{NF}_4\text{PtF}_6$  also decomposes into the starting reagents but, in addition, some of the  $\text{PtF}_6$  formed on initial decomposition decomposes further into  $\text{PtF}_4$  and  $\text{F}_2$ .

(C) The decomposition reaction can be understood if the cation and anion are written  $\text{NF}_3-\text{F}^+$  and  $\text{MF}_x-\text{F}^-$ , where M may be Sb, As, P, or B. When the bonds to  $\text{F}^+$  and to  $\text{F}^-$  are broken, these entities can then form  $\text{F}_2$ . In the case of  $\text{NF}_4\text{PtF}_6$ , the anion must be written  $\text{PtF}_6-\text{e}^-$ , and the electron reacting with  $\text{F}^+$  to form F and subsequently  $\text{F}_2$  completes the description. This mode of decomposition permits us to speculate on the stability of salts such as the hypothetical  $\text{NF}_4\text{ClF}_4$  or  $\text{NF}_4\text{BrF}_6$ . The alkali metal salts of  $\text{ClF}_4^-$  and  $\text{BrF}_6^-$  decompose in HF, while the similar salts of  $\text{BF}_4^-$  do not. This indicates that the fluoride ion is less strongly held in  $\text{ClF}_4^-$  and  $\text{BrF}_6^-$  than in  $\text{BF}_4^-$ . Consequently, we can conclude that the  $\text{NF}_4^+$  salts of the interhalogen anions will be less stable than  $\text{NF}_4\text{BF}_4$ , but how much less stable is certainly not known nor is it possible to predict this from presently known data. It can be argued, however, that the alkali metal  $\text{ClF}_4^-$  and  $\text{BrF}_6^-$  salts are quite stable thermally,<sup>11</sup> and that this thermal stability is a sufficient basis for expecting the corresponding  $\text{NF}_4^+$  salts to be satisfactorily stable. Thus it is our recommendation that experimental efforts to synthesize  $\text{NF}_4\text{ClF}_4$ ,  $\text{NF}_4\text{BrF}_6$ , and possibly other interhalogen-containing anions be undertaken.

(C) The decomposition of  $\text{NF}_4\text{ClO}_4$  above  $-27.5^\circ\text{C}$  and the observed instability of  $\text{NF}_4\text{SO}_3\text{F}$  at  $-78^\circ\text{C}$  and above can be understood, at least in part, by invoking the structure  $\text{NF}_3-\text{F}^+$ . The reactions form either  $\text{FClO}_4$

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or  $\text{FOSO}_2\text{F}$  as though  $\text{F}^+$  were reacting directly with a localized negative charge on the anion. We have concluded that this decomposition behavior below room temperature probably is to be expected of most, if not all, other oxyanions. We therefore do not recommend further work on coupling  $\text{NF}_4^+$  with an oxyanion in the near future.

(C)One of the indices we have used to predict stability of an anion in the presence of  $\text{NF}_4^+$  is the relative ease of directly fluorinating the anion in the form of its salts or as the acid. Our results on  $\text{NF}_4^+$  and oxyanions have led us to believe that salts or acids fluorinated by fluorine will be much more easily fluorinated by  $\text{NF}_4^+$ . Conversely, it appears that ionic compounds not easily fluorinated by fluorine might contain anions that will be stable when coupled with  $\text{NF}_4^+$ . On the basis of this simple index, we have selected several compounds containing anions that might very well be stable when coupled with  $\text{NF}_4^+$  and have recommended further study of these.

(C)The metathesis reactions in which  $\text{NF}_4\text{ClO}_4$  and  $\text{NF}_4\text{HF}_2$  were synthesized should be viewed as a generally applicable method for synthesis of energetic oxidizers. This type of reaction in liquid HF or in interhalogens may very well find application to syntheses involving energetic cations other than  $\text{NF}_4^+$  and to anions not yet studied during our search for new  $\text{NF}_4^+$  compounds. We intend to use the solubility information and knowledge of compatibility of various pertinent compounds in HF and in interhalogen solvents to pursue the synthesis of solid oxidizers.

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## III EXPERIMENTAL SECTION

### A. Direct Synthesis Reactions

(C) Experimental procedures for the synthesis of  $\text{NF}_4^+$  salts from  $\text{NF}_3$ ,  $\text{F}_2$ , and Lewis acids were described in our report AFRPL-TR-66-326, November 14, 1966, and in a published paper.<sup>1</sup> The report includes drawings of apparatus not given in the paper.

(U) These articles discuss the handling of  $\text{NF}_3$  and  $\text{F}_2$  in the vacuum line and describe a safe procedure for dealing with  $\text{F}_2$  under high pressure, but little comment is devoted to the manipulation of  $\text{SbF}_5$  and the other anion precursors used in the preparation of  $\text{NF}_4^+$  salts.  $\text{SbF}_5$  has a low vapor pressure and can be transferred only very slowly. It also reacts with fluorides on the walls of the vacuum system and forms  $\text{SbF}_6^-$  and, we feel certain,  $\text{Sb}_2\text{F}_{11}^-$  and possibly  $\text{Sb}_3\text{F}_{16}^-$  salts. These salts can plug the line, hydrolyze when water is introduced as a reactant, probably interact with HF, and in general yield a system that is difficult to evacuate and may require cleaning. Thus,  $\text{SbF}_5$  should be distilled from its container into a buret and from the buret into the reactor through the shortest path. This can be done in a small subsystem that can be easily cleaned.

(U)  $\text{AsF}_5$  forms arsenate salts in an  $\text{F}_2$  passivated Monel metal line but forms no complex arsenate salts analogous to the antimony system. In addition, these simple hexafluoroarsenates resist hydrolysis. Thus  $\text{AsF}_5$  could be handled in the vacuum line without difficulty. Its quantity was determined by PV measurements which were adequate for our purposes.

(C)  $\text{PtF}_6$  was synthesized by burning electrically heated platinum wire in an atmosphere of fluorine contained in a vessel cooled to liquid nitrogen temperature.<sup>12</sup> The excess  $\text{F}_2$  was removed and discarded, and the  $\text{PtF}_6$  was isolated, weighed, and transferred to the reaction vessel. The transfer was made through the shortest path possible, the system having been thoroughly passivated whenever the line or parts of the line were exposed to the atmosphere. We observed no decomposition of the  $\text{PtF}_6$  during manipulation.

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(C)  $\text{PF}_5$  and  $\text{BF}_3$  were handled by the same technique used for  $\text{AsF}_5$ . It seems unlikely, however, that these two reagents are of interest in preparing  $\text{NF}_4^+$  salts by the direct synthesis method because of the low yields.

## B. Metathesis Reactions

(C) Experimental details of importance in metathesis reactions include handling of solvents and the nature of the apparatus. The solvents used in the present work were HF and several interhalogens. Extensive effort was required, with each solvent, to obtain pure material suitable for use with  $\text{NF}_4^+$  salts. When purified, HF,  $\text{ClF}_3$ ,  $\text{ClF}_5$ ,  $\text{BrF}_5$  and  $\text{IF}_5$  are colorless;  $\text{BrF}_3$  is yellow.

(U) Preparation of anhydrous HF involves several steps that can be hazardous. The first of these steps in which difficulty might be encountered is the isolation of the desired quantity from the steel container in which the HF is received. HF reacts with the container to form hydrogen which must be removed to facilitate vacuum transfer and to avoid possible reaction at a later stage when the HF is treated with fluorine. In this work, HF and  $\text{H}_2$  are passed into a specially designed copper trap cooled with liquid nitrogen. HF is frozen out, while most of the hydrogen is pumped away. The trap is built so that the inlet line from the HF container extends halfway to the bottom of the trap. When the HF level in the trap rises to the bottom of the inlet tube, the inlet tube is plugged with frozen HF and the transfer stops. Another hazard is avoided by the design of the trap. The HF expands by a factor of about 1.5 on warming from  $-196^\circ$  to room temperature; thus if the HF were melted in an enclosed volume too small to contain the resulting volume of liquid, enormous pressure would develop and burst the container. Use of the metal trap also permits rapid heat transfer, rapid and apparently complete condensation and freezing of the HF, and a high rate of transfer.

(U) When melted, a portion of the HF in the trap is transferred slowly into a Kel-F vessel at  $-196^\circ\text{C}$ . Transfer must be sufficiently slow that no liquid forms in the metal lines. If liquid forms, impurities are

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entrained in the HF and collect in the Kel-F vessel. Frost on the lines indicates the probable presence of liquid HF. However, if the transfer is carried out so that HF is vaporized in the trap, passes through the line in the vapor phase, and is recondensed only in the Kel-F vessel, the product should be colorless. Again, care should be taken to assure that only about half the volume of the vessel is filled with HF. Although the Kel-F vessel is cooled with liquid nitrogen, the rate of heat transfer is sufficiently low and the rate of input of HF is high enough that the HF condenses as a liquid and is frozen only after transfer is stopped and the vessel has been allowed to stand at  $-196^{\circ}\text{C}$  for about half an hour. Pumping on the frozen HF apparently removes any hydrogen that might remain.

(U)To avoid possible contamination with water that can diffuse through the walls of the Kel-F vessel, the HF is transferred immediately to a copper vessel in which it is treated with fluorine. The mixture is allowed to stand overnight, and the fluorine and other volatiles are removed by pumping on the HF solid at  $-196^{\circ}\text{C}$ .

(C)Small amounts of HF for use in metathesis reactions are transferred as needed from the copper storage vessel. However, if the vacuum line has been passivated with respect to an interhalogen, a new effect is observed. The HF interacts with the passivation products in the line and the liquid in the receiver is colored. We have assumed that the colored HF contains impurities that would probably react with  $\text{NF}_4^{+}$  salts. To avoid this, we have treated the vacuum line with HF and  $\text{F}_2$  until the liquid HF isolated is colorless. The treatment requires several batch-wise additions of HF and  $\text{F}_2$  and may consume as much as a day's work. Colorless liquid HF, when obtained as outlined above, reacts negligibly or not at all with  $\text{NF}_4^{+}$  salts.

(C)To obtain interhalogens suitable for metathesis reactions requires passivation of the system with respect to the interhalogen and subsequent removal of products of the passivation reactions. We have noted that a system apparently passivated with respect to fluorine is not passive toward an interhalogen. In addition, a system passive with respect to one interhalogen is not necessarily passive with respect to another.

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However, we have worked out a technique that enables us to obtain solvent that does not react with  $\text{NF}_4^+$  salts and that can be used for all the interhalogens we have studied. The technique involves batchwise addition of, for example,  $\text{IF}_5$  to the vacuum line until no non-condensables are formed. When this condition is achieved, products of the passivation reaction are still in the line. These products are removed sufficiently well by treatment with fluorine and evacuation of the system.

(C) On passivation of the system and removal of impurities,  $\text{IF}_5$  or other interhalogen is condensed into a Kel-F storage vessel. This vessel is equipped with a stirring magnet and contains an excess of  $\text{KF}$  to remove  $\text{HF}$ .  $\text{BrF}_3$  forms a stable, solid salt with  $\text{KF}$  but not with  $\text{CsF}$ . This will be discussed below. The storage vessel is enclosed in a polyethylene bag containing a desiccant to prevent diffusion of water into the system. The interhalogen is condensed into a reaction vessel containing  $\text{NF}_4^+$  salt and does not react with the  $\text{NF}_4^+$ .

(C)  $\text{BrF}_3$ , in our work contaminated with  $\text{BrF}_5$ , was purified (in part at least) by trap-to-trap distillation and was subsequently mixed with an excess of  $\text{CsF}$ .  $\text{CsBrF}_4$  and  $\text{CsBrF}_6$  formed on standing with stirring for 48 hours, after which the  $\text{BrF}_3$  was recovered by warming the salts with a heat gun.  $\text{CaBrF}_4$  decomposed readily on warming and  $\text{BrF}_3$  was recovered.  $\text{NF}_4\text{SbF}_6$  was soluble in and did not react with  $\text{BrF}_3$  obtained in this manner.

(U) The apparatus for the metathesis reactions is shown schematically in Fig. 1, and has been discussed briefly in Section II. Details of the apparatus involve the type of fittings and connectors used and the design of the filter system.

(C) The filter system was evolved in stages throughout this work. We found that Chemplast Company Zitex brand paper, composed of Kel-F and Teflon, was compatible with  $\text{NF}_4^+$  salts in  $\text{HF}$  solution and with  $\text{BrF}_5$ . The first paper available was a coarse grade; finer grades were later obtained. The filter paper was supported on a perforated Kel-F disk and held in place by a snap ring. Pressure drops across the filter paper developed when the vacuum system was pressurized with nitrogen to

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check for gross leaks or when HF was admitted. Occasionally, the filter paper was pulled out of the snap ring by the pressure change. When finer grades of paper were used, the pressure drops almost invariably caused displacement of the paper and a new design was required. When the paper was supported between two perforated Kel-F disks, the filter remained intact and filtered adequately as well.

(U)Figure 2 shows the fittings and vessels used for the apparatus. The Kel-F must be machined very slowly with spray cooling to prevent overheating the plastic. One vessel, which was machined without such cooling, formed deep stress cracks when placed in liquid nitrogen. Vessels made subsequently with cooling have not cracked except after extensive use. It should be noted that the metathesis reaction assembly was quite expensive.

(C)The procedure for using this apparatus is described in the following outline of the preparation of  $\text{NF}_4\text{BF}_4$ . The parts of the subsystem are thoroughly degreased with trichloroethylene, assembled, attached to the vacuum line, filled with 2 atm of nitrogen, and tested for leaks with a soap solution. When leak-free under these conditions, the unit is tested with a helium leak detector. It should be noted that helium diffuses slowly through the FEP Teflon Tubing (1/4" o.d., 1/8" i.d.). This may be observed by placing a plastic bag around the subsystem and filling the bag with helium. After one to two minutes, the leak detector registers an enormous leak. When the plastic bag and thus the source of helium is removed, the helium in the system is removed only very slowly. This is due in part, at least, to the slow rate of diffusion through Teflon. Consequently, helium leak testing of this system must be carried out rather quickly, avoiding long exposure of the Teflon to the stream of helium.

(U)When leak-free, the T system was placed in the dry box.

(C)A 5 g sample of  $\text{NF}_4\text{SbF}_6$  was added to the filter tube in the dry box, and a 3 g sample of CsF was added to the receiving tube. Both tubes contained Teflon-coated stirring bars. The 3 g of CsF was a 29% excess. The tubes were attached to the T and HF was added using the vacuum line.

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About 5 ml of HF was added to each sample. After stirring, the CsF solution was added to the  $\text{NF}_4\text{SbF}_6$  solution. A heavy white precipitate formed. Some HF was distilled back to wash the receiving tube. Part of the HF was distilled off, concentrating the  $\text{NF}_4\text{HF}_2$  solution to reduce the total  $\text{CsSbF}_6$  content in solution. The solution was filtered through the extrafine-grade Teflon filter paper. About 3 ml of solution passed through the filter.

(C) Another 5 ml of HF was distilled into the  $\text{NF}_4\text{HF}_2$  solution. An excess of  $\text{BF}_3$  at 50 psi was placed above the solution and the solution was stirred for 30 min. The solution was cooled to  $-78^\circ\text{C}$  and stirred for a few minutes, then allowed to warm and stirred further. The cooling and stirring process was carried out two more times after which the  $\text{BF}_3$  and HF were removed and the solids were pumped on to remove traces of HF.

(C) The receiving tube had collected 2.19 g of product (theory: 2.71 g).

The T system was returned to the dry box and a filter cap was added to the tube with the  $\text{NF}_4\text{BF}_4$ . A receiving tube, prepassivated with  $\text{BrF}_5$ , as was the filter cap, was attached to the T.

(C) The vacuum system was passivated with  $\text{BrF}_5$  before  $\text{BrF}_5$  was added to the sample. A sample of  $\text{BrF}_5$  was added to the  $\text{NF}_4\text{BF}_4$  and the mixture was stirred for 1-1/2 hrs. Some solid remained undissolved. The solution was filtered, yielding a clear filtrate. Total  $\text{BrF}_5$  in the solution was 5.3 ml.

(C) The  $\text{BrF}_5$  was distilled off and the solid was pumped on overnight. The recovery was 0.99 g of  $\text{NF}_4\text{BF}_4$ ; also, some was lost in the arms of the T.

(C) Both hydrolysis and pyrolysis indicate that the final product consisted of about 92%  $\text{NF}_4\text{BF}_4$  with 8% of  $\text{NF}_4\text{SbF}_6$ .

## C. Infrared Spectra

(C) The infrared spectra of  $\text{NF}_4\text{SbF}_6$ ,  $\text{NF}_4\text{AsF}_6$ , and  $\text{NF}_4\text{PtF}_6$  are given in Figs. 3, 4, and 5, respectively. These spectra were obtained on a few milligrams of the salt dispersed in 350 mg of finely divided salt;

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this mixture was then pressed in a pellet die into a transparent plate. Either KCl or KF was used.  $\text{NF}_3$  appears in all spectra we have obtained by this technique. Its presence is the result of decomposition of the  $\text{NF}_4^+$  salt during the pressing of the pellet. Since the pellet, while being pressed, cannot be expected to reach temperatures at which thermal decomposition can occur, the  $\text{NF}_3$  must arise from reaction with impurities in the KF or KCl or with KCl itself. We obtained some spectroscopic-grade KF, compared spectra of  $\text{NF}_4\text{SbF}_6$  obtained in KCl and in KF, and observed that much less  $\text{NF}_3$  was present in the KF matrix.

(C) The KCl was reagent-grade salt that was precipitated rapidly from a saturated solution with concentrated HCl, dried in a vacuum oven for a week, and stored in the dry box. Spectra of blank KCl pellets showed that a small amount of water was present if the die was not leak-free. The same was true of KF. In addition, when spectra of  $\text{NF}_4^+$  salts were studied, several bands due to bifluoride were observed, which indicated reaction with  $\text{H}_2\text{O}$ . These bands were less significant in KF, corresponding to the smaller amount of  $\text{NF}_3$  present in these pellets.

(C) The bifluoride absorption bands are quite intense, and we estimate that if 0.5% of the  $\text{NF}_4^+$  salt were converted to bifluoride by hydrolysis, the bifluoride band at 1220 to 1230  $\text{cm}^{-1}$  would be easily seen. This band has been assigned by Christie et al.,<sup>13</sup> to  $\text{NF}_4^+$ , but we feel this is open to question.

(U) The die used in pressing pellets is a specially hardened unit with 0.5" diameter pistons. The driver piston is tungsten carbide alloy, which occasionally splits under the pressure employed, i.e., 45,000 pounds of thrust in a press with a 2" diameter ram. The die containing the pressed plate is returned to the dry box where the pellet is removed. The pellet is placed in a sealed cell to prevent contact with atmospheric moisture. The cell consists of a holder containing two silver chloride windows separated by a washer having O-rings on each face. The pellet fits inside the washer.

(U) Sample preparation includes grinding a weighed quantity of the salt matrix to a very fine powder in a mortar, grinding the sample to a fine

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powder in a separate mortar, weighing the sample, and then grinding the sample and matrix together.

## D. NMR Spectra

(U) $\text{NF}_4^+$  salts are generally quite soluble in HF and give good  $\text{F}^{19}$  nmr spectra in this solvent. With HF, glass or quartz tubes cannot be used; it is common practice to employ a Kel-F nmr tube. In this work, these are machined from 8" long Kel-F tubing, 1/4" o.d., 1/8" i.d. Seven inches of this length is reduced in diameter to 0.190 inch. The narrow end is sealed with the aid of a small flame.

(U)The tubing is degreased, attached to a valve, connected to the vacuum line, and passivated. After passivation, the assembly is leak-tested to be certain that the heat-sealed end is properly sealed. The assembly is then placed in the dry box where a weighed sample of salt is placed in the tube. On reassembly and removal from the dry box, the unit is attached to the vacuum line and leak-tested again, and HF is added to the desired level. The tube is cooled to  $-196^\circ\text{C}$  and is heat-sealed well above the level of the HF. When the HF melts, a leak in the new seal can be easily detected as a stream of white vapor. Refreezing the solution permits further attempts to seal the tube. When a seal has been obtained the ends of the tube, which may have become distorted during the sealing process, can be reduced to the proper diameter either by filing or by working the melted plastic. The latter method is best carried out with the contents frozen.

(U)These tubes are spinnable in the nmr spectrometer. However, the spectroscopist should handle the sample carefully in view of its contents.

(C)Spectra as illustrated in Figs. 6, 7, and 8 were obtained on a Varian Associates HA-100 spectrometer at 94.6 Mc. The field was usually scanned from the HF line to the  $\text{F}_2$  line. However, only the portion showing HF,  $\text{CFCl}_3$ , and  $\text{NF}_4^+$  is included. In the spectrum of  $\text{NF}_4\text{AsF}_6$ , the quadruplet due to  $\text{AsF}_6^-$  is detectable at about 70 ppm from  $\text{CFCl}_3$ . No lines due to  $\text{SbF}_6^-$  or  $\text{PtF}_6^-$  were seen. When the salt is largely  $\text{NF}_4\text{Sb}_2\text{F}_{11}$ , the HF and SbF peaks merge to give a very broad line. Thus, if the  $\text{SbF}_6^-$  concentration were very high, we expect that it would appear

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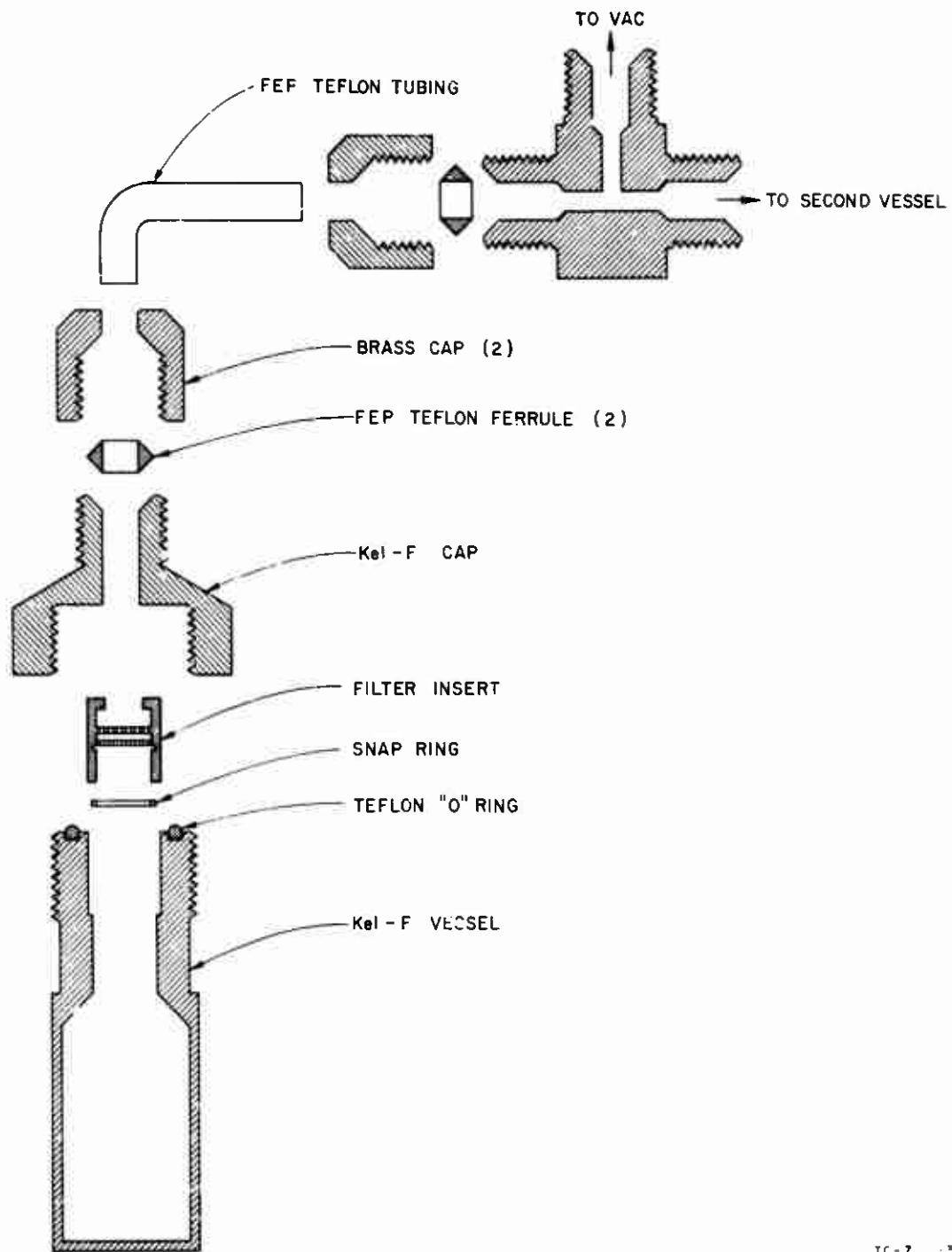


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under the sidebands downfield of HF. The  $\text{CFCl}_3$  line was obtained by the substitution method. Spectra were usually scanned both with and without  $\text{CFCl}_3$  reference in order to determine whether weak lines could be observed in the vicinity of the  $\text{CFCl}_3$  line.

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FIG. 2 1:1 SCALE DRAWING OF METATHESIS REACTION VESSEL AND FILTER

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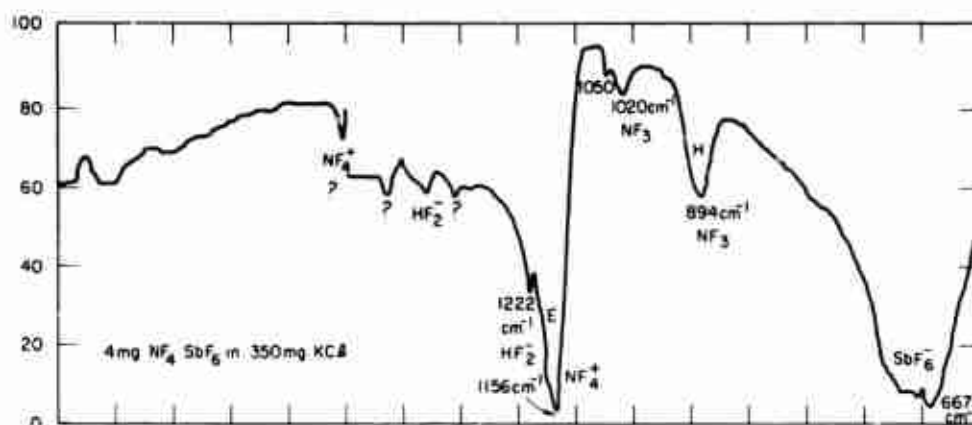


FIG. 3 INFRARED SPECTRUM OF  $\text{NF}_4\text{SbF}_6$

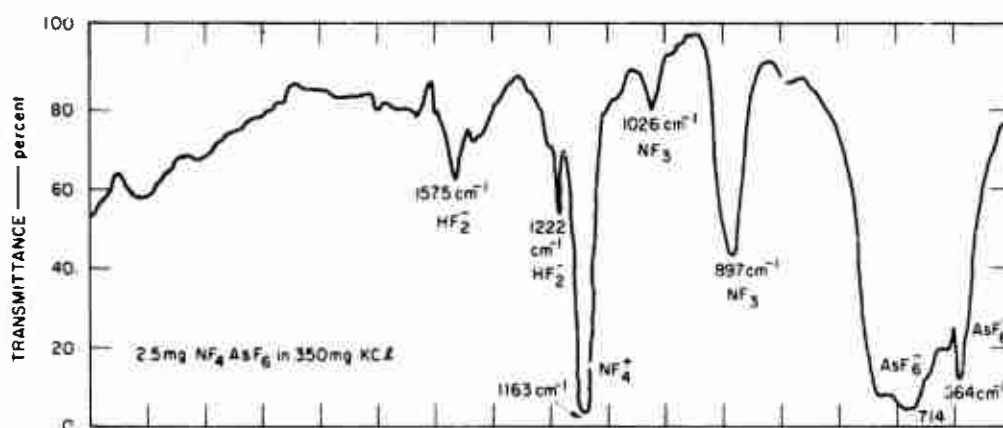


FIG. 4 INFRARED SPECTRUM OF  $\text{NF}_4\text{AsF}_6$

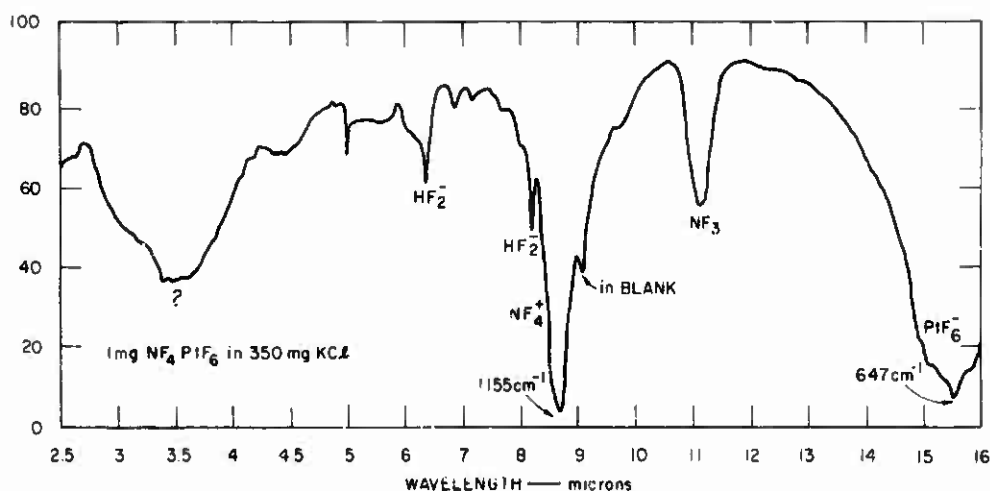


FIG. 5 INFRARED SPECTRUM OF  $\text{NF}_4\text{PF}_6$

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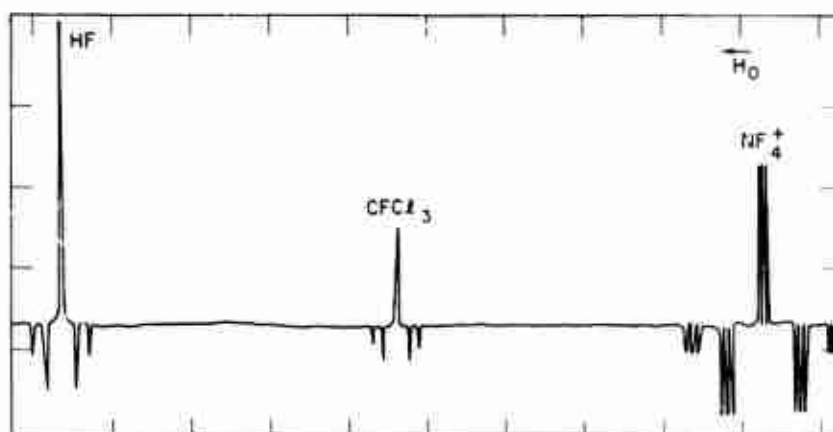


FIG. 6  $^{19}\text{F}$  nmr SPECTRUM OF  $\text{NF}_4\text{SbF}_6$  (37.5 wt% in HF)

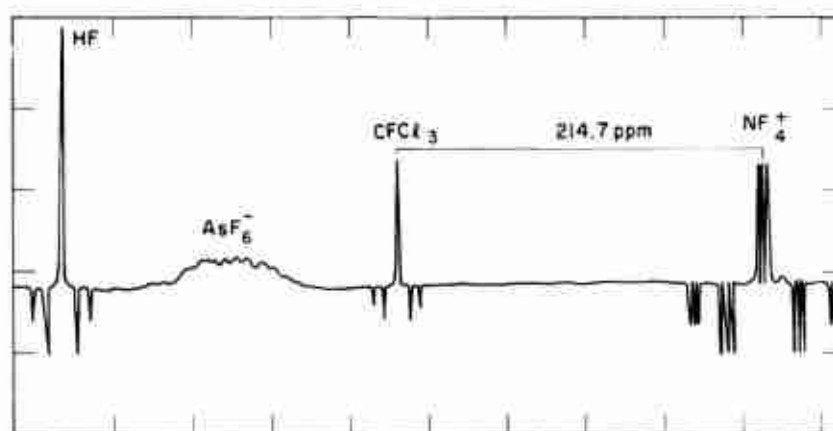


FIG. 7  $^{19}\text{F}$  nmr SPECTRUM OF  $\text{NF}_4\text{AsF}_6$  (ca 0.5 gm/cc of HF)

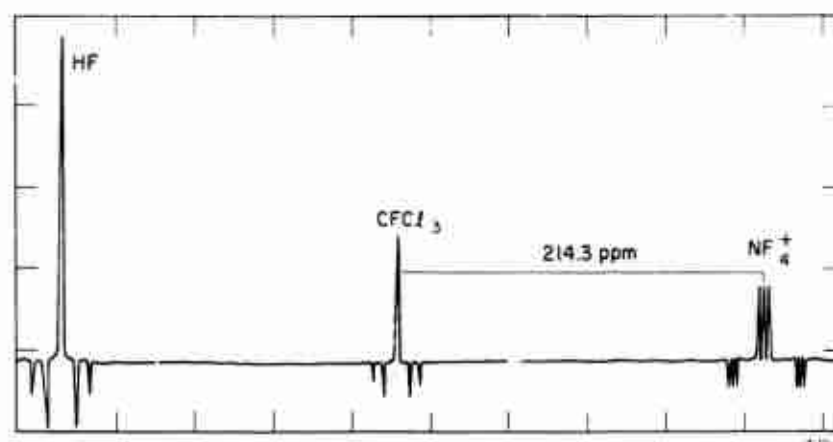


FIG. 8  $^{19}\text{F}$  nmr SPECTRUM OF  $\text{NF}_4\text{PF}_6$  (concentration ca 100 mg/cc of HF)

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13. ABSTRACT		
<p>Synthesis of <math>\text{NF}_4^+</math> salts has been carried out by two general methods. Direct synthesis reactions of <math>\text{NF}_3</math>, <math>\text{F}_2</math>, and a series of Lewis acids at high pressures and moderately elevated temperatures have been used to produce a series of <math>\text{NF}_4^+</math> salts having fully fluorinated anions. Metathesis reactions in liquid HF have been used to produce a number of new <math>\text{NF}_4^+</math> salts including some with oxygen-containing anions. (C)</p> <p>The rate of reaction to form <math>\text{NF}_4^+</math> salts in direct synthesis depends on the acidity of the Lewis acid. Thus, <math>\text{SbF}_5</math> forms <math>\text{NF}_4\text{SbF}_6</math> in good yield, <math>\text{AsF}_5</math> produces the arsenate in moderate yield, <math>\text{PF}_5</math> forms <math>\text{NF}_4\text{PF}_6</math> in very low yield, and <math>\text{BF}_3</math> produces only a trace of <math>\text{NF}_4\text{BF}_4</math>, if any. It was concluded that compounds less acidic than <math>\text{PF}_5</math> in HF would be unlikely to form <math>\text{NF}_4^+</math> salts by direct synthesis. This was confirmed when <math>\text{ClF}_3</math> and <math>\text{ClF}_5</math> did not yield the corresponding salts, <math>\text{NF}_4\text{ClF}_4</math>, or <math>\text{NF}_4\text{ClF}_6</math>, on heating <math>\text{NF}_3</math>, <math>\text{F}_2</math>, <math>\text{ClF}_3</math>, and <math>\text{ClF}_5</math> at high pressure for extended periods of time. (C)</p> <p>In addition to <math>\text{NF}_4\text{SbF}_6</math>, <math>\text{NF}_4\text{AsF}_6</math>, and <math>\text{NF}_4\text{PF}_6</math>, a fourth salt, <math>\text{NF}_4\text{PtF}_6</math>, was formed by direct synthesis in the reaction:</p> $\text{NF}_3 + 1/2 \text{F}_2 + \text{PtF}_6 \rightarrow \text{NF}_4\text{PtF}_6 \quad (\text{C})$ <p>This salt was characterized by nmr and infrared spectroscopy, hydrolysis, and elemental analysis of the hydrolysate. (C)</p> <p><math>\text{NF}_4\text{SbF}_6</math> has proved to be the most useful in metathesis reactions. Its synthesis is complicated by the formation of varying amounts of the complex fluoroanti-</p>		

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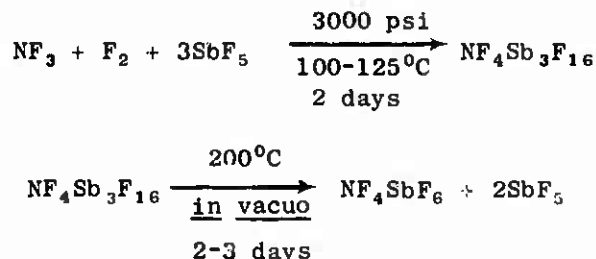
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<p><math>\text{NF}_4\text{SbF}_6</math></p> <p>Metathetical Reactiona in Liquid HF and Interhalogens</p> <p>Solubilities</p> <p>Inorganic Oxidizers</p>						

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monate anions,  $\text{Sb}_2\text{F}_{11}^-$  and  $\text{Sb}_3\text{F}_{16}^-$ , as well as formation of contaminants formed by reaction of  $\text{F}_2$  and  $\text{SbF}_5$  with the Monel reaction vessel. The optimum conditions found for synthesis of  $\text{NF}_4\text{SbF}_6$  involve:



Products ranging in purity from 96 to 99.5% have been obtained. Monel-antimonate impurities were removed by dissolving  $\text{NF}_4\text{SbF}_6$  in HF and filtering out the insoluble metal salts. (C)

Fully characterized  $\text{NF}_4\text{SbF}_6$  has been used as a reagent in a number of metathesis reactions forming new salts. A typical reaction is:



Similar reactions have been used to form  $\text{NF}_4\text{HF}_2$ ,  $\text{NF}_4\text{SO}_3\text{F}$ ,  $\text{NF}_4\text{NO}_3$ , and  $\text{NF}_4\text{BF}_4$ . The perchlorate decomposes to  $\text{NF}_3$  and  $\text{FClO}_4$  above  $-27.5^\circ\text{C}$ , the bifluoride is unstable at  $-44^\circ\text{C}$  and above, the fluorosulfonate is unstable at  $-78^\circ\text{C}$  and above, the nitrate is decomposed in HF solution, but  $\text{NF}_4\text{BF}_4$  is quite stable. (C)

$\text{NF}_4\text{CN}$  could not be formed owing to decomposition of the alkali metal cyanide to HCN in liquid HF and to the reaction of cyanide with the interhalogen solvent  $\text{BrF}_5$ . The similar decomposition of  $\text{K}_2\text{SiF}_6$  in HF led to an attempt to synthesize  $(\text{NF}_4)_2\text{SiF}_6$  in  $\text{BrF}_5$ . No reaction occurred on mixing  $\text{NF}_4\text{SbF}_6$  with  $\text{K}_2\text{SiF}_6$  in  $\text{BrF}_5$ . The lack of reaction indicated that one or both of the starting reagents dissolved without dissociation into ionic species. (C)

Several alkali metal salts of the  $\text{ClF}_4^-$  and  $\text{BrF}_6^-$  anions were synthesized. In HF, these decompose to form alkali metal bifluorides and the corresponding interhalogen. They are, however, moderately soluble in  $\text{BrF}_5$ . It is expected that this solvent will permit determining whether the salts  $\text{NF}_4\text{ClF}_4$  and  $\text{NF}_4\text{BrF}_6$  can be synthesized. (C)

An effort was made to synthesize  $\text{NF}_4\text{BF}_4$  in a purity sufficient for determining heats of formation. The highest purity obtained was 96.1%. The impurities have not yet been determined. (C)

A number of solubility studies were carried out in support of work on metathesis reactions. Solubilities of a number of pertinent compounds in HF,  $\text{BrF}_5$ ,  $\text{IF}_5$ , and  $\text{BrF}_3$  are reported and discussed. (U)

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